Ozone and organic nitrates over the eastern United States: Sensitivity to isoprene chemistry

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Abstract

We implement a new isoprene oxidation mechanism in a global 3-D chemical transport model (GEOS-Chem). Model results are evaluated with observations for ozone, isoprene oxidation products, and related species from the ICARTT aircraft campaign over the eastern United States in summer 2004. The model achieves an unbiased simulation of ozone in the boundary layer and the free troposphere, reflecting canceling effects from recent model updates for isoprene chemistry, bromine chemistry, and HO_2 loss to aerosols. Simulation of the ozone-CO correlation is improved relative to previous versions of the model and this is attributed to a lower and reversible yield of isoprene nitrates, increasing the ozone production efficiency (OPE) per unit of nitrogen oxides ($NO_x \equiv NO + NO_2$). The model successfully reproduces the observed concentrations of organic nitrates ($\sum$ANs) and their correlations with HCHO and ozone. $\sum$ANs in the model is principally composed of secondary isoprene nitrates, including a major contribution from nighttime isoprene oxidation. The correlations of $\sum$ANs with HCHO and ozone then provide sensitive tests of isoprene chemistry and argue in particular against a fast isomerization channel for isoprene peroxy radicals. $\sum$ANs can provide an important reservoir for exporting NO_x from the US boundary layer. We find that the dependence of surface ozone on isoprene emission is positive throughout the US, even if NO_x emissions are reduced by a factor of 4. Previous models showed negative dependences that we attribute to erroneous titration of OH by isoprene.

1. Introduction

Isoprene (2-methyl-1,3-butadiene), the most important nonmethane volatile organic compound (NMVOC) emitted by vegetation, affects tropospheric ozone, OH (the main tropospheric oxidant), and aerosols in complex ways. It has a lifetime of about one hour against oxidation by OH. The resulting oxidation products lead to the formation of ozone, an effective greenhouse gas and air pollutant. Isoprene also reacts with the nitrate radical (NO_3) at night, with important implications for global budget of nitrogen oxides ($NO_x \equiv NO + NO_2$) and therefore ozone. The successive oxidation steps of isoprene produce a range of multifunctional organic compounds that can go on to form secondary organic aerosols (SOA) with implications for climate and public health. The ICARTT aircraft campaign provided a detailed characterization of boundary layer chemistry across the isoprene-rich eastern US in July–August 2004 (Fehsenfeld et al., 2006; Singh et al., 2006). We use here aircraft observations from this campaign, interpreted with a global 3-D chemical transport model (GEOS-Chem), to better understand the importance of isoprene chemistry for tropospheric ozone and SOA precursors.

Daytime oxidation of isoprene is initialized by its reaction with OH, leading to the production of peroxy radicals ($ISOPO_2$). In the presence of NO_x, $ISOPO_2$ reacts with NO leading to the production of organic nitrates by a minor branch. These nitrates may act as a sink for both HO_x ($HO_x \equiv H + OH +$ peroxy radicals) and NO_x, and therefore affect global and regional ozone budgets (von Kuhlmann et al., 2004; Fiore et al., 2005; Horowitz et al., 2007; Wu et al., 2007; Ito et al., 2009; Perring et al., 2009a; Paulot et al., 2012; Xie et al., 2012). Laboratory data indicate a yield of first-generation organic nitrates from isoprene oxidation ranging from 7% to 12% (Sprengnether et al., 2002;

Giacopelli et al., 2005; Patchen et al., 2007; Paulot et al., 2009a; Lockwood et al., 2010). A model interpretation of the ICARTT data by Horowitz et al. (2007) indicated a smaller yield (4%). Isoprene nitrates are partly recycled back to NO_x upon further oxidation, leading to further complication in their role as a sink or reservoir for NO_x (Horowitz et al., 2007; Ito et al., 2009; Paulot et al., 2009a; Perring et al., 2009a; Paulot et al., 2012). They may serve as nitrogen reservoir to export boundary layer NO_x to rural and remote atmospheres (Atlas, 1988; Horowitz et al., 1998; Neff et al., 2002).

In the absence of NO_x, $ISOPO_2$ is assumed in standard mechanisms to be converted to organic hydroxyperoxides ISOPOOH (Jacob and Wofsy, 1988), leading to titration of OH. However, observations from a number of field campaigns show no such OH titration (Carslaw et al., 2001; Tan et al., 2001; Thornton et al., 2002; Lelieveld et al., 2008; Ren et al., 2008; Hofzumahaus et al., 2009; Pugh et al., 2010; Stone et al., 2010; Whalley et al., 2011). Several mechanisms have been proposed to explain this discrepancy, including OH regeneration via oxidation of epoxydiols formed from the oxidation of ISOPOOH based on laboratory studies (Paulot et al., 2009b), and fast isomerization of $ISOPO_2$ based on theoretical studies (Peeters et al., 2009; Peeters and Müller, 2010). Measurements of OH concentrations by the standard Laser Induced Fluorescence (LIF) technique may be biased high due to internally generated OH from oxidation of biogenic VOCs (Mao et al., 2012). After correcting for this effect, Mao et al. (2012) find good agreement between model and observations when OH regeneration from oxidation of epoxydiols (Paulot et al., 2009b) and laboratory-based slow isomerization of $ISOPO_2$ (Crounse et al., 2011) are included in the model.

Besides daytime oxidation, nighttime oxidation of isoprene by NO_3 contributes significantly to the budget of organic nitrates (von Kuhlmann et al., 2004; Horowitz et al., 2007; Xie et al., 2012). This pathway is initialized by addition of NO_3 to one of the double bonds of isoprene, followed by production of organic nitrates with high yield (65-85%) (Paulson and Seinfeld, 1992; Perring et al., 2009b; Rollins et al., 2009). These organic nitrates can degrade in a matter of hours to more stable forms of organic nitrates, leading to the formation of SOA (Rollins et al., 2009).

Isoprene chemistry is of particular importance in affecting summertime ozone over the eastern US (Jacob et al., 1993), with important implications for air quality management. Both global and regional chemical transport models tend to overestimate summertime surface ozone over the eastern US by 10-20 ppb (Murazaki and Hess, 2006; Yu et al., 2007; Lin et al., 2008; Fiore et al., 2009; Yu et al., 2010; Rasmussen et al., 2012). Fiore et al. (2005) suggested that this problem might be due to incorrect representation of isoprene sources and chemistry.

The ICARTT aircraft campaign is a unique resource for testing models of isoprene chemistry and the impact of isoprene on ozone. It provided a detailed characterization of boundary layer chemistry across the eastern US in July–August 2004 (Fehsenfeld et al., 2006; Singh et al., 2006). Two aircraft were deployed with comprehensive chemical payloads, including measurements of isoprene and several of its oxidation products (Fried et al., 2008; Perring et al., 2009a; Warneke et al., 2010). Previous analyses of isoprene chemistry using ICARTT data have been presented by Horowitz et al. (2007), Perring et al. (2009a), and Xie et al. (2012) with a focus on isoprene nitrates, and by Stavrakou et al. (2010) with a focus on HO_x.

A number of previous studies have applied GEOS-Chem to simulation of the ICARTT data, including evaluation with observations of NO_x and ozone (Hudman et al., 2007; Liang et al., 2007; Hudman et al., 2009), CO (Turquety et al., 2007; Hudman et al., 2008), HCHO (Millet et al., 2006) and aerosols (Heald et al., 2006; Fu et al., 2009; Drury et al., 2010). In particular, Hudman et al. (2007) found that the lightning NO_x source inferred from the ICARTT data was much larger than expected, and Hudman et al. (2008) found the need for a 60% reduction in CO emissions relative to the National Emission Inventory (NEI 99) from the US Environmental Protection Agency (EPA). Hudman et al. (2009) indicated no significant bias in their simulation of ozone over the eastern US after the lightning correction, and neither did a subsequent GEOS-Chem study by Zhang et al. (2011). However, those model versions assumed an unreasonably high yield of isoprene nitrates (18%) and that isoprene nitrates behaved like a terminal sink for NO_x.

Here we implement in GEOS-Chem a state-of-science isoprene chemistry mechanism based on Paulot et al.(2009a) and Paulot et al. (2009b), along with other updates, and evaluate the simulation of ozone, isoprene oxidation products, and related chemical correlations during ICARTT. From there we gain insights into the organic nitrates produced from isoprene oxidation and their role in ozone chemistry, and we discuss the sensitivity of summertime surface ozone to isoprene emissions.

2. GEOS-Chem Model

2.1 General description

GEOS-Chem is a global 3-D chemical transport model driven by assimilated meteorological observations from the Goddard Earth Observing System (GEOS-5) of the

NASA Global Modeling and Assimilation Office (GMAO) (Bey et al., 2001). We apply here GEOS-Chem version 9-01-03 (http://www.geos-chem.org) to simulation of the ICARTT period (July 1st - Aug 15th 2004). The GEOS-5 meteorological data have 6-h temporal resolution (3-h for surface variables and mixing depths) with 0.5° × 0.667° horizontal resolution and 72 vertical layers from the surface to 0.01 hPa. We regrid here the meteorological data to 2° × 2.5° for input to GEOS-Chem. The model is initialized with a 1-year simulation from June 2003 to June 2004 with 4° × 5° resolution, and from June 2004 on with 2° × 2.5° resolution. Boundary layer mixing in GEOS-Chem uses the non-local scheme (Holtslag and Boville, 1993) implemented by Lin and McElroy (2010). Stratospheric ozone is simulated with a linearized ozone (Linoz) algorithm described by McLinden et al. (2000).

Biogenic emission of isoprene follows the process-based Model of Emissions of Gases and Aerosols from Nature (MEGAN) inventory (Guenther et al., 2006; Millet et al., 2008; Barkley et al., 2011) with monthly mean leaf area index from the MODIS satellite instrument (Myneni et al., 2007). The resulting North American isoprene emission is 10.2 TgC for June-August 2004 (65W to 130W, 20N to 50N), in line with an independent estimate of 7.1-11.6 TgC inferred from satellite data for formaldehyde (Millet et al., 2008).

Anthropogenic emission inventories in GEOS-Chem include EPA NEI-05 for the US, CAC for Canada (http://www.ec.gc.ca/pdb/cac/cac_home_e.cfm), BRAVO for Mexico (Kuhns et al., 2005), EMEP for Europe (Vestreng and Klein, 2002), and Streets et al. (2006) for East Asia. We reduce CO emissions in the NEI-05 inventory by 53% following Hudman et al.(2008). This reduction is consistent with other estimates of US

CO emissions based on atmospheric observations (Parrish, 2006; Miller et al., 2008; Miller et al., 2012; LaFranchi et al., 2013). For the rest of the world we use the EDGAR emission inventory for CO, NO_x, and SO_2 (Olivier and Berdowski, 2001), and the RETRO emission inventory for volatile organic compounds (VOCs) (Schultz et al., 2007). All anthropogenic emissions are scaled to 2004 based on energy statistics (van Donkelaar et al., 2008).

Lightning NO_x emissions are calculated as a function of GEOS-5 cloud top height and rescaled to match OTD/LIS climatological observations (Murray et al., 2012). The global lightning source is imposed to be 6 Tg N yr^{-1} (Martin et al., 2007), with higher NO_x yields per flash at mid-latitudes than in the tropics (Hudman et al., 2007). We use monthly biomass burning emissions from the Global Fire Emission Database version 3 (GFED-v3) (van der Werf et al., 2010). Forest fire plumes transported from Alaska and western Canada were important in the free troposphere during ICARTT (Turquety et al., 2007; Pfister et al., 2008). Soil NO_x emissions are computed using a modified version of the Yienger and Levy (1995) algorithm with canopy reduction factors as described in Wang et al. (1998).

Dry deposition in GEOS-Chem is calculated using a standard resistance-in-series model (Wesely, 1989), in which the surface resistances for gases are determined by their Henry's law constants and surface reactivities. We revised the reactivity of all oxygenated VOCs including ketones, aldehydes, organic peroxides and organic nitrates, to be the same as ozone following Karl et al. (2010). We also include wet and dry deposition of isoprene hydroperoxide and epoxydiols with Henry's law constants of 1.7×10^6 M atm^{-1} and 1.3×10^8 M atm^{-1} following Marais et al. (2012). Wet deposition is

described by Liu et al. (2001) for water soluble aerosols and by Amos et al. (2012) for gases. It includes wet scavenging in convective updrafts as well as grid-resolved first-order rainout and washout.

The standard GEOS-Chem simulation of ozone-NO_x-HO_x-VOC chemistry is described by Mao et al. (2010), with more recent implementation of bromine chemistry (Parrella et al., 2012). The chemical mechanism includes updated recommendations from the Jet Propulsion Laboratory (Sander et al., 2011) and the International Union of Pure and Applied Chemistry (http://www.iupac-kinetic.ch.cam.ac.uk). In addition, we included an improved HO_2 aerosol reactive uptake suggested by Mao et al. (2013). We also increased the NO_3 aerosol reactive uptake coefficient γ from 1×10^{-4} (Jacob, 2000) to 0.1, as suggested by recent laboratory and field studies (Gross et al., 2009; Tang et al., 2010; Fry et al., 2011; Brown and Stutz, 2012; Lee et al., 2013). The treatment of isoprene oxidation is described in the following subsection.

2.2 Chemical mechanism for isoprene oxidation

A focus of this work is to use the ICARTT observations to test our model mechanism for isoprene chemistry. This new mechanism differs significantly from the original isoprene oxidation mechanism in GEOS-Chem described in Horowitz et al. (1998). The full mechanism is describd at http://wiki.seas.harvard.edu/geos-chem/index.php/New_isoprene_scheme. Figure 1 illustrates the treatment of first-generation isoprene oxidation by OH. Oxidation under the high-NO_x regime mainly follows Paulot et al. (2009a). It is initialized by OH addition at 1 and 4 positions, resulting in a pool of β and δ-hydroxyl peroxy radicals ($ISOPO_2$) with yields of 71% and

29% respectively. In the presence of NO_x, the degradation of β-hydroxyl $ISOPO_2$ leads to the production of HCHO (66%), methylvinylketone (MVK) (40%) and methacrolein (MACR) (26%) with a small yield of β-hydroxyl isoprene nitrates (ISOPNB) (6.7%). Reaction of δ-hydroxyl $ISOPO_2$ with NO leads to the formation of δ-hydroxyl isoprene nitrates (ISOPND) (24%). The total first-generation isoprene nitrates yield (11.7%), from ISOPND (7.0%) and ISOPNB (4.7%) respectively, is in line with other laboratory studies as described above. The fates of ISOPNB and ISOPND are discussed below.

Under low NO_x conditions, $ISOPO_2$ can follow either of two pathways. One is to react with HO_2 to form isoprene hydroxyperoxides (ISOPOOH) with a small production of HCHO, MVK and MACR (4.7%, 7.3%, 12% respectively) (Paulot et al., 2009b), largely consistent with a recent study by Liu et al. (2012). Most of ISOPOOH reacts with OH to produce epoxydiols and quantitatively regenerate OH (Paulot et al., 2009b). Another pathway is the unimolecular isomerization of $ISOPO_2$ (1,6-H shift) (Peeters et al., 2009; Peeters and Müller, 2010), leading to the production of hydroperoxyaldehydes (HPALDs). The subsequent fate of HPALDs is dominated by photolysis, with a 100% yield of OH (Wolfe et al., 2012). We do not consider the 1,5-H shift as it is expected to be unimportant (Da Silva et al., 2010; Crounse et al., 2011). The rate constant of 1,6-H shift isomerization is still under debate (Peeters et al., 2009; Peeters and Müller, 2010; Crounse et al., 2011). We adopt the rate constant from Crounse et al.(2011), which is lower than the original one from Peeters et al. (Peeters et al., 2009; Peeters and Müller, 2010) by a factor of ~50. As we will see in section 4, the lower rate constant affords a better simulation of organic nitrate measurements in ICARTT.

219 The subsequent fate of ISOPND and ISOPNB is mainly via reactions with OH and ozone
220 because of the remaining C=C bond. Paulot (2009a) suggested that ISOPND and
221 ISOPNB have photochemical lifetimes against oxidation by OH of 1h and 7h respectively
222 (OH=3×10^6 molecule cm^{-3} at 298 K). Lockwood et al. (2010) suggested photochemical
223 lifetimes against oxidation by ozone of 2h and 4h respectively (ozone = 60 ppbv), which
224 is 5-10 times shorter than the previous value suggested by Giacopelli et al. (2005). As a
225 result, these nitrates are degraded in a matter of hours, leading to the formation of a series
226 of secondary organic nitrates, including methylvinylketone nitrates (MVKN),
227 methacrolein nitrates (MACRN), ethanal nitrate (ETHLN) and propanone nitrate
228 (PROPNN), as shown in Figure 2. Reactions of ISOPND and ISOPNB with ozone can
229 also produce these secondary organic nitrates, and this is mainly from the decomposition
230 of primary ozonides that are initially formed by the addition of ozone across the C=C
231 bond (Baker et al., 2002). These secondary organic nitrates are more stable than the
232 primary ones due to the lack of a C=C bond. MVKN, MACRN, and ETHLN have
233 lifetimes of 17 h, 2 h, 9 h against oxidation by OH (OH=3×10^6 molecule cm^{-3} at 298 K),
234 and PROPNN is mainly lost through photolysis with a global mean lifetime of 13 d in
235 GEOS-Chem. The degradation of these secondary organic nitrates is assumed to return
236 NO_x with a yield of 55% (Paulot et al., 2009a).

237 Nighttime isoprene oxidation is updated from Xie et al.(2012), which is largely based on
238 the chamber study by Rollins et al. (2009). This new treatment assumes 70% yield of
239 first generation carbonyl nitrates from the isoprene + NO_3 reaction. These nitrates can be
240 further oxidized by NO_3, leading to the formation of secondary organic nitrates (Figure 3).
241 For simplification, we lump here all secondary organic nitrates from nighttime isoprene

oxidation into one lumped alkyl nitrate (R_4N_2), which has a global mean lifetime of 5 d against OH oxidation and photolysis in GEOS-Chem.

Several additional updates are included in this new mechanism. First, we implemented the isomerization of methacrolein peroxy radicals ($MACRO_2$) based on experiments by Crounse et al. (2012). Second, we updated the reaction rate of HO_2 with > C_2 peroxy radicals to the expression in Saunders et al. (2003), leading to an increase of factor 2 for HO_2 + $ISOPO_2$ at 298 K. Third, we updated OH regeneration for the reactions of HO_2 with acetyl peroxy ($CH_3C(O)O_2$) and acetonyl peroxy ($CH_3C(O)CH_2O_2$) radicals based on laboratory measurements (Hasson et al., 2004; Jenkin et al., 2007; Dillon and Crowley, 2008). Fourth, the reaction of isoprene with ozone was modified following the Master Chemical Mechanism v3.2 (Jenkin et al., 1997; Saunders et al., 2003).

3. Simulation of ozone and related species

Here we use the ICARTT observations to evaluate our new isoprene oxidation mechanism implemented in GEOS-Chem. There were two aircraft in the field, the NASA DC-8 and the NOAA WP-3D (Fehsenfeld et al., 2006; Singh et al., 2006). We mostly focus on data from the DC-8, which provided regional coverage over the eastern US, whereas the WP-3D often targeted urban plumes in the Northeast (Warneke et al., 2007). However, we use the MVK+MACR observations from the WP-3D as these measurements were not made on the DC-8. We exclude biomass burning and urban plumes (CH_3CN > 225 ppt or HCN > 425 ppt or NO_2 > 4 ppb or NO_x/NO_y > 0.4 mol mol^{-1}) which would not be represented properly on the scale of the model (Hudman et al., 2007). We also exclude stratospheric air as diagnosed by ozone/CO > 1.25 mol mol^{-1}. All

comparisons between model and observations use model output sampled along the flight tracks and at the flight time with 15-min time resolution. Almost all of the data were collected between 08:00 and 18:00 local time.

Figure 4 (top panels) compares observed and simulated mean ozone concentrations in the boundary layer (0 – 1.5 km). A regression for the ensemble of the data shows no significant bias (lower left panel). The model largely captures the spatial pattern of boundary layer ozone, but with a relatively low correlation, likely due to the inaccuracy in locating point emission sources. The model overestimates boundary layer ozone in the Southeast US by 3 – 5 ppbv but has no bias over the Northeast. The small ozone bias over the Southeast could be due to several factors including excessive convection in the model over the Gulf of Mexico (Fiore et al., 2002), and omission of terpene compounds that may act as additional NO_x sinks through formation of organic nitrates (Browne and Cohen, 2012; Pratt et al., 2012).

In the analysis that follows we mainly focus on the data collected over land. Figure 5 shows the mean 0-4 km vertical profiles of ozone, isoprene, CO, HCHO, peroxyacetyl nitrate (PAN), HNO_3, NO_x, and MVK+MACR concentrations measured by the aircraft and simulated by the model. The spatial distributions of summertime HCHO, CO, and NO_y over the eastern US during ICARTT have been examined in previous GEOS-Chem studies (Millet et al., 2006; Hudman et al., 2007; Hudman et al., 2008). As shown in Figure 5, the vertical gradient of ozone between the boundary layer and the free troposphere is well reproduced by the model. CO is also well simulated, reflecting the adjustment of anthropogenic emissions as recommended by Hudman et al.(2008). We discuss the other species below.

Isoprene measured by the DC-8 decreases from 500 pptv near the surface to 20 pptv at 3 km, reflecting its short photochemical lifetime. Values measured by the WP-3D are lower, reflecting the Northeast sampling bias. As MVK, MACR and HCHO are major first generation products from isoprene oxidation under high NO_x conditions (Figure 1), they all show a rapid decrease from boundary layer to 3 km, consistent with isoprene. Millet et al. (2006) previously showed that isoprene was the dominant source of HCHO variability during ICARTT. The model provides overall a good simulation of the observed mean profiles. The yield of HCHO from isoprene oxidation appears to be relatively insensitive to the choice of mechanism (Marais et al., 2012), but the yield of MVK+MACR is sensitive to the rate constant of $ISOPO_2$ isomerization, as MVK and MACR are not produced by that pathway (Figure 1). In a sensitivity simulation using the fast isomerization of $ISOPO_2$ (Peeters et al., 2009; Peeters and Müller, 2010) we find mean MVK + MACR concentrations of 100 pptv in the boundary layer, much lower than observed.

Mean observed NO_x decreases from 700 pptv near the surface to 50 pptv at 3 km. The model agrees with observations within 30%. Oxidation of NO_x produces HNO_3, PAN, and other organic nitrates (to be discussed in section 4). Simulated HNO_3 in the free troposphere is too high, which could reflect insufficient scavenging. PAN is simulated without bias. We find that isoprene is the main VOC precursor for PAN, consistent with previous model studies for the eastern US (Horowitz et al., 1998) as well as observed correlations with other peroxyacylnitrates (Williams et al., 1997).

The most recent previous evaluation of the GEOS-Chem ozone simulation over the US was by Zhang et al.(2011), who also found no significant bias. That simulation used v8-

310 02-03 of GEOS-Chem. Since then, several objective improvements have been made to
311 GEOS-Chem that have had significant consequences for the ozone simulation
312 (http://www.geos-chem.org): (1) decrease in isoprene nitrate yield (from 18% to 11.7%)
313 and partial recycling of NO_x (section 2.2), (2) inclusion of tropospheric bromine
314 chemistry (Parrella et al., 2012), (3) heterogeneous loss of HO_x radicals (Mao et al.,
315 2013), and (4) correction of the diurnal cycle of NO_x emissions. For the eastern US
316 boundary layer and free troposphere in summer, (1) causes a 3-5 ppbv increase in ozone
317 in the model. However, the resulting positive bias is effectively corrected by (2)-(4), each
318 of which decreases ozone in the above conditions by 1-3 ppbv. This highlights the
319 importance of canceling errors in model simulations of ozone. Further constraints can be
320 obtained by correlations of ozone with related species, as discussed below.

321 ## 4. Organic nitrates and relationship with HCHO and ozone

322 Perring et al. (2009a) made measurements of total organic nitrates other than
323 peroxyacylnitrates ($RONO_2$, hereinafter ∑ANs) aboard the DC-8 during ICARTT. As
324 ∑ANs is mainly expected to include isoprene nitrates under the ICARTT conditions
325 (Beaver et al., 2012), this provides an opportunity to evaluate the simulation of isoprene
326 nitrates in GEOS-Chem. Analysis of the ICARTT ∑ANs data has been presented
327 previously in several studies. Perring et al. (2009a) found good correlation between
328 observed HCHO and ∑ANs in the boundary layer. Horowitz et al. (2007) found that the
329 vertical profile of ∑ANs and the ozone-∑ANs correlation could be best reproduced by a
330 4% yield of isoprene nitrates with 40% recycling efficiency. Xie et al. (2012) applied the
331 treatment of isoprene nitrates from Paulot et al. (2009a) to the CMAQ regional air quality

model, but they find an overestimate of ∑ANs by 30% in their model. We here examine organic nitrates and their relationship with HCHO and ozone in GEOS-Chem.

Figure 6 shows the mean vertical profile of ∑ANs during ICARTT. Concentrations decrease from 200 pptv near the surface layer to 50-100 pptv in the free troposphere, both in observations and in the model. In contrast to Xie et al. (2012), we show very little overestimation of ∑ANs in the model. This is likely due to different treatment of organic nitrates produced from NMVOCs other than isoprene, as they find that only 60% of ∑ANs is from isoprene oxidation in their model, in contrast to more than 90% in our model. We also find that the vertical profile of $\sum$ANs is insensitive to the deposition rates of ISOPND and ISOPNB because of their short photochemical lifetimes. A sensitivity simulation using slower reaction rates with ozone (Giacopelli et al., 2005) shows little difference in the vertical profile of $\sum$ANs, as ISOPND is mainly oxidized by OH. A sensitivity simulation using the fast isomerization of $ISOPO_2$ (Peeters et al., 2009; Peeters and Müller, 2010) produces less than 100 pptv $\sum$ANs in the boundary layer.

We see from Figure 6 that ∑ANs in the model is mainly contributed by the second generation of isoprene nitrates, i.e., PROPNN, MVKN+MACRN and R_4N_2 (Figure 2). This reflects the short lifetime of the first-generation isoprene nitrates against oxidation by OH and ozone. For the same reason, MVKN+MACRN decline rapidly in the free troposphere where most of ∑ANs is contributed by the longer-lived R_4N_2 and PROPNN species. Oxidation of isoprene by NO_3 accounts for 80% of R_4N_2 in the model, emphasizing the need for better understanding of this chemistry (Grossenbacher et al., 2001; Brown et al., 2009; Beaver et al., 2012; Kwan et al., 2012).

Perring et al. (2009a) pointed out that the observed HCHO - ∑ANs correlation provides an additional constraint on the bulk yield of isoprene nitrates, due to the co-production of HCHO and ∑ANs from isoprene oxidation under the high-NO_x regime (Figure 1). As shown in Figure 7, the model reproduces successfully the observed continental boundary layer correlation in ICARTT. Fast isomerization of $ISOPO_2$ (Peeters et al., 2009) underestimates the ∑ANs yield. Despite the large fraction of R_4N_2 in ∑ANs, we find that the variability of ∑ANs in boundary layer is largely determined by the daytime products of isoprene oxidation.

∑ANs and ozone are co-produced from RO_2 + NO reactions, so that one would expect a strong correlation between the two (Flocke et al., 1991; Horowitz et al., 2007; Ito et al., 2009). This correlation has been used to constrain ozone production efficiency and photochemical aging in urban conditions (Rosen et al., 2004; Perring et al., 2010; Farmer et al., 2011). We find that the observed correlation in ICARTT (Figure 7) is reproduced by GEOS-Chem. Similar to ∑ANs vs. HCHO, this correlation cannot be reproduced by the model using the fast isomerization of $ISOPO_2$.

The yield of first generation nitrates (11.7%) in our mechanism is considerably higher than the yield derived by Horowitz et al. (2007). Using the same observational dataset, they found that ∑ANs vs. ozone correlation can best match their model with 4% yield of isoprene nitrates. With 8% yield, they overestimated boundary layer ∑ANs by 40%. This can be attributed to their assumption that secondary organic nitrates are inert and the slow RO_2 + HO_2 rate used. In fact, a large fraction of secondary nitrates in our model, such as ETHLN and MACRN (Figure 3), can degrade in a matter of hours returning NO_x, with little contribution to ∑ANs.

Secondary organic nitrates from daytime and nighttime isoprene oxidation provide an important mechanism for exporting NO_x from the US boundary layer. We show in Table 1 that nitrogen is more efficiently exported as ∑ANs than as PAN, partly due to their longer photochemical lifetimes. Long-range transport of ∑ANs is supported by measurements of $\geq C_3$ alkyl nitrates in rural and remote atmospheres (Atlas, 1988; Russo et al., 2010).

5. Ozone – CO correlation

Observations in polluted regions show positive ozone-CO correlations in summer, and these correlations can be related to the ozone production efficiency per unit NO_x emitted (OPE) through the NO_x/CO emission ratio (Horowitz et al., 1998; Hudman et al., 2009). Chin et al. (1994) reported a regression slope (dO_3/dCO) of 0.28-0.32 mol mol^{-1} at three eastern U.S. sites in 1988-1992. Parrish et al. (1998) reported dO_3/dCO of 0.28-0.40 for 1991-1994 at four sites in Atlantic Canada. Hudman et al. (2009) found higher observed dO_3/dCO of 0.41-0.46 in the continental boundary layer during ICARTT, reflecting decadal changes in U.S. CO and NO_x emissions as well as an apparent increase in the OPE. Their GEOS-Chem simulation indicated a smaller dO_3/dCO (0.34 – 0.36), likely due to an excessive yield of isoprene nitrates as discussed above.

The bottom right panel of Figure 4 shows our simulated ozone-CO correlations for the boundary layer DC-8 aircraft flight tracks (0 – 1.5 km altitude) in the afternoon (1100 – 1700 LT), compared to observations. The dO_3/dCO value is determined by the slope of the reduced-major-axis regression line, with errors determined by nonparametric bootstrap resampling. The observations indicate $dO_3/dCO = 0.43 \pm 0.03$, as previously

reported by Hudman et al. (2009), but here the relationship is better reproduced by the model (0.39 ± 0.02), reflecting the new isoprene mechanism as well as HO_2 aerosol uptake (lowering OH and thus increasing the lifetime of NO_x). The slope degrades to 0.33 in a sensitivity simulation using the Peeters et al. (2009) rate constant of $ISOPO_2$ isomerization, mainly due to a faster oxidation of NO_x through higher OH.

6. Sensitivity of surface ozone to isoprene emissions

Isoprene emissions may change rapidly on decadal time scales due to ecosystem evolution and changes in forestry practices (Purves et al., 2004; Guenther et al., 2006; Heald et al., 2009; Wu et al., 2012). Understanding the effect of these changes in isoprene emission is critical for air quality management. Models disagree even in the sign of the response of summertime surface ozone in the eastern US to isoprene emissions, varying from a decrease (Fiore et al., 2005; Wu et al., 2008; Wu et al., 2012) to an increase (Horowitz et al., 1998; Sanderson et al., 2003). This has been attributed to the discrepancies between models in the yield of isoprene nitrates (Wu et al., 2007), NO_x recycling efficiency from isoprene nitrates (Ito et al., 2009) and the relative magnitude of isoprene and NO_x emissions (Fiore et al., 2005).

Figure 8 shows our computed change of mean afternoon (1300 – 1700 LT) surface ozone concentrations during July 2004 as a result of increasing current isoprene emissions by 25% in the model. At current level of anthropogenic NO_x emissions (for the year of 2004), we find an ozone increase of 2 – 4 ppbv with the new implemented isoprene mechanism (top left panel). When anthropogenic NO_x emissions are reduced to 50% of current level, we find that the sensitivity of ozone to increasing isoprene emissions is reduced by about a

factor of 2 (top right panel). Reduction of NO_x emission to 25% of current level shows further decrease of the ozone sensitivity to isoprene emission (not shown), although the sensitivity does not become negative. With the isoprene chemistry applied in Zhang et al. (2011) that assumed a high yield of isoprene nitrates (18%) without recycling of NO_x, we find similar negative sensitivity of ozone to isoprene emissions (bottom panels in Figure 8), consistent with previous model studies as described above. This reflects in part the importance of isoprene ozonolysis as a sink for ozone under low-NO_x conditions because of OH titration (Mickley et al., 2001; Fiore et al., 2005). As pointed out above, such OH titration by isoprene in models appears inconsistent with observations. Nevertheless, our work indicates that reducing anthropogenic NO_x emissions to improve ozone air quality significantly reduces the sensitivity of ozone to isoprene emissions.

7. Conclusions

We implemented a state-of-science isoprene chemistry mechanism in GEOS-Chem, based on Paulot et al.(2009a) and Paulot et al. (2009b), along with other updates. This mechanism was evaluated with observations from the NASA DC8 and NOAA WP3D aircraft during the ICARTT campaign over the eastern US in the summer of 2004.

Models have a general tendency to overestimate surface ozone in the eastern US (Fiore et al., 2009). The previous GEOS-Chem simulation of Zhang et al. (2011) was unbiased relative to observations but it assumed an excessive yield of isoprene nitrates serving as terminal sinks for NO_x. Our improved representation of isoprene chemistry increases ozone over the eastern US by 3-5 ppbv, and this is compensated by other model improvements including bromine chemistry and HO_2 loss to aerosols. Thus the GEOS-

Chem ozone simulation remains unbiased relative to observations, in the boundary layer as well as the free troposphere. Simulation of the observed ozone-CO correlation is improved relative to previous versions of GEOS-Chem and this is attributed to the reduced yield of isoprene nitrates.

ICARTT observations of total organic nitrates other than PANs (∑ANs) are well reproduced in the model, including vertical profiles and correlations with HCHO and ozone. This provides a sensitive test of the isoprene oxidation mechanism and argues in particular against a fast isomerization pathway for the $ISOPO_2$ radical. ∑ANs in the model is mainly composed of secondary organic nitrates, including a large fraction from nighttime oxidation of isoprene. These secondary nitrates provide an important pathway for exporting NO_x from the US boundary layer, exceeding the export of PANs. Better understanding of nighttime oxidation of isoprene and of the fate of the resulting organic nitrates is needed.

Our improved representation of isoprene chemistry yields a positive dependence of ozone on isoprene emissions throughout the US, in contrast to previous model studies that found a negative dependence particularly in the southeastern US. We attribute this difference to OH titration by isoprene in previous models, promoting ozone loss by isoprene ozonolysis. Our new mechanism avoids this OH titration, for which observations show no evidence. Nevertheless, we find that the sensitivity of ozone to isoprene emissions decreases as NO_x emissions decrease. This may have important implications for air quality management as well as for understanding ozone concentrations in the preindustrial atmosphere.

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Figures and Tables

Table 1 NO_y budget in eastern U.S. Boundary Layer for July 2004

Species	Emission	Chemical (P-L)	Dry Deposition	Wet Deposition	Net Export
NO_x	386	-337	44	------	5
PANs[a]		24	13	------	11
∑ANs					
ANs [b]		18	7.4	3.6	7
R_4N_2 [c]		10	0.5	-------	10
HNO_3		277	180	110	-3

We define the eastern U. S. boundary layer as 62.5° – 97.5 °W, 24° – 52 °N, and from the surface to approximately 1.8 km altitude (below 800 hPa). Budget terms are in GgN.

[a] PANs include peroxyacetyl nitrate (PAN), peroxymethacryloyl nitrate (PMN) and peroxypropionylnitrate (PPN).

[b] ANs include δ-hydroxyl isoprene nitrates (ISOPND), β-hydroxyl isoprene nitrates (ISOPNB), methacrolein nitrates (MACRN), methylvinylketone nitrates (MVKN), propanone nitrate (PROPNN) and ethanal nitrate (ETHLN).

[c] Nighttime isoprene oxidation contributes to 80% of R_4N_2 production.

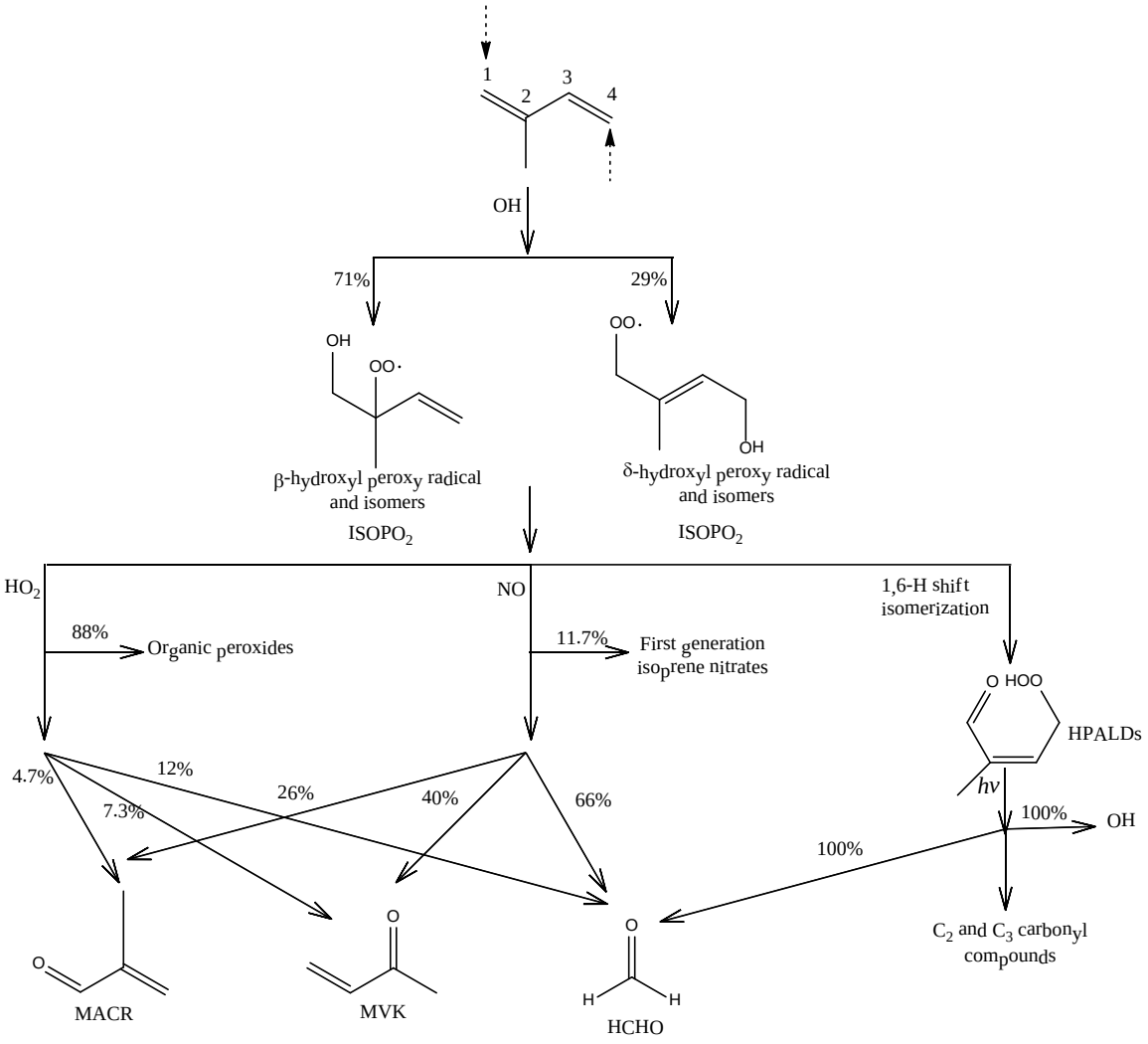


Figure 1 Schematic of the first stage of the isoprene oxidation mechanism initiated by OH.

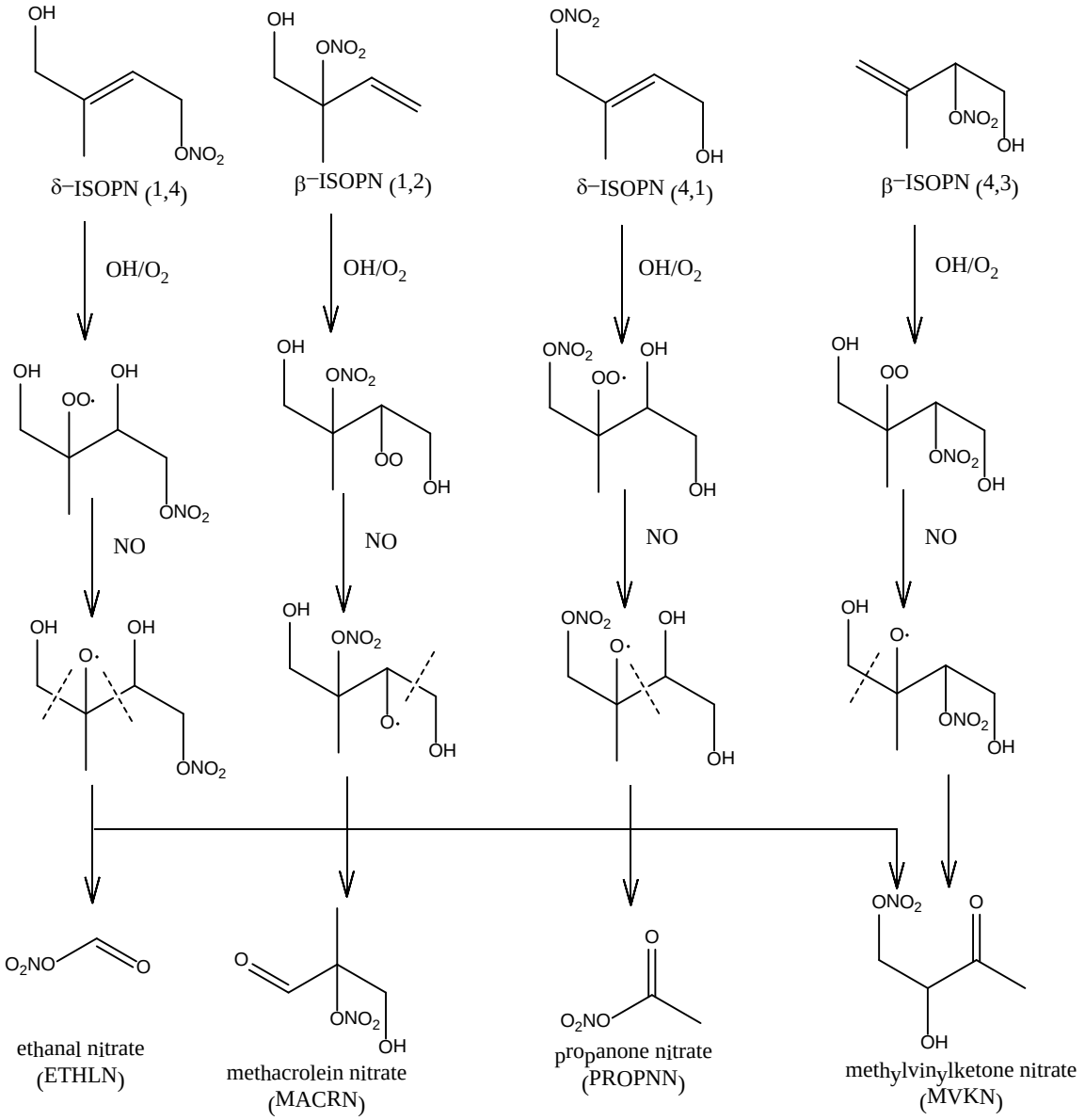
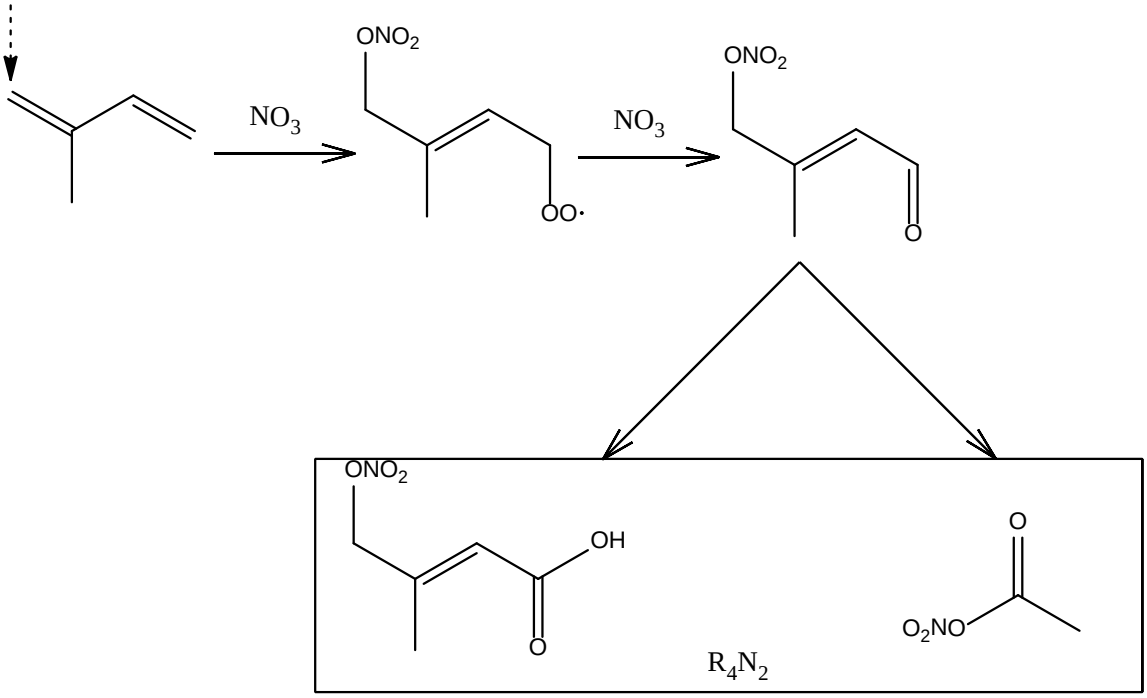


Figure 2 Schematic of the oxidation of isoprene nitrates by OH following Paulot et al. (2009a).



493

494 Figure 3 Partial schematic of isoprene oxidation by NO_3 following Rollins et al. (2009)
495 and Xie et al. (2012).

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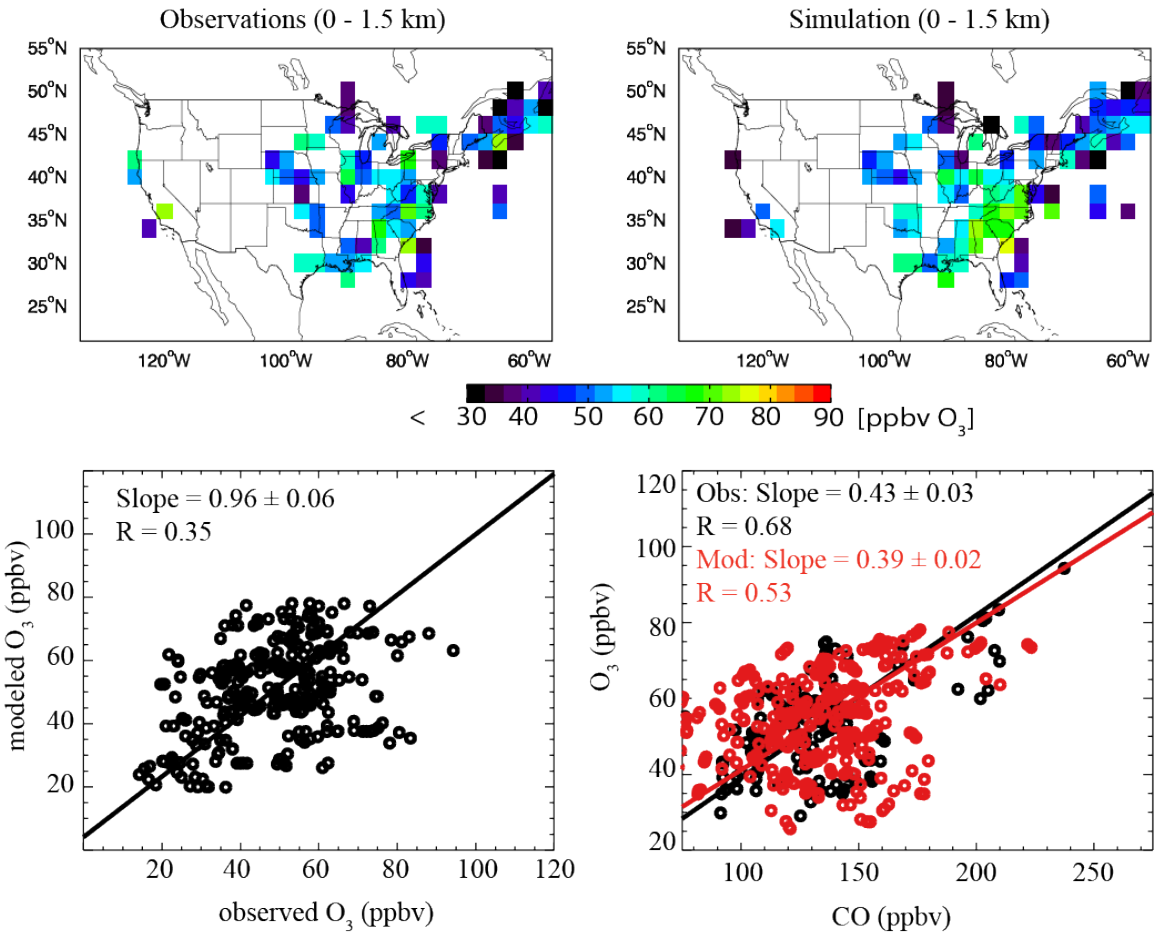
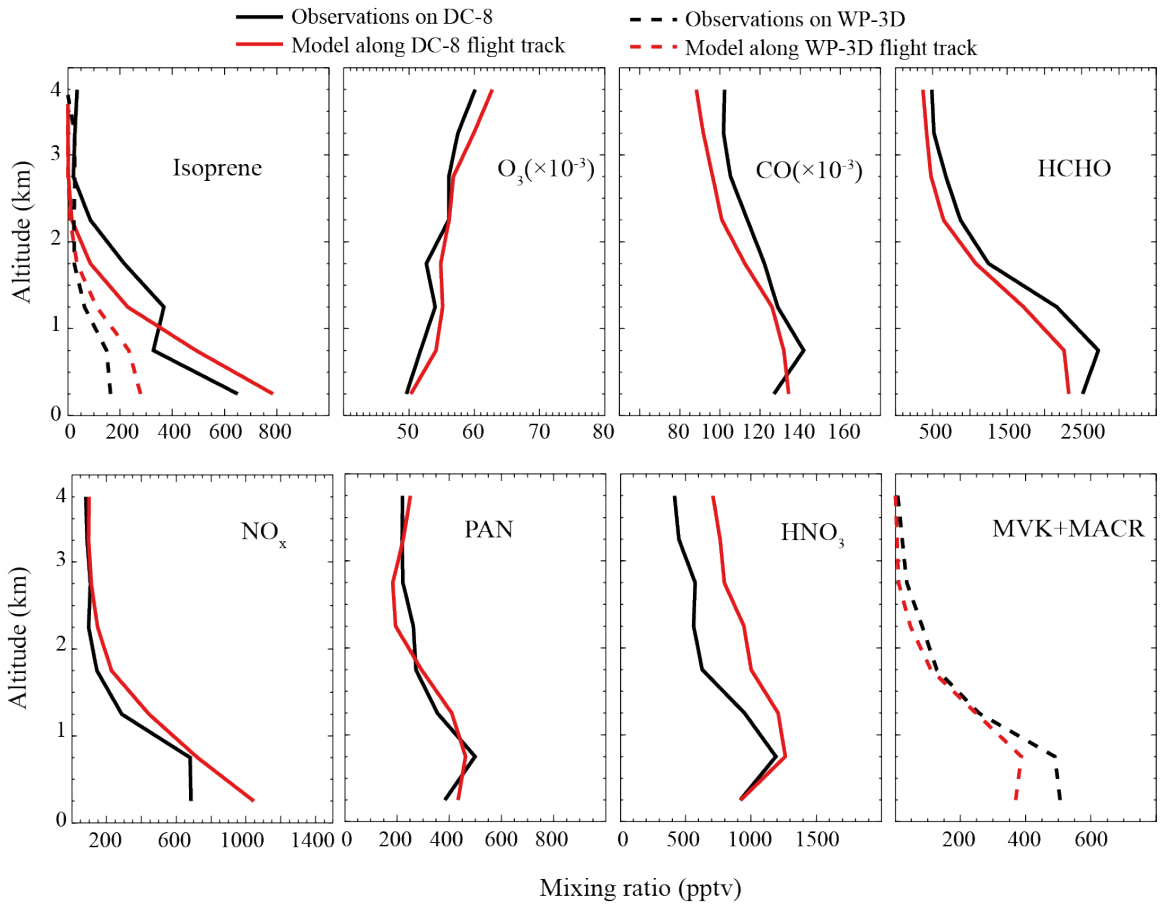


497

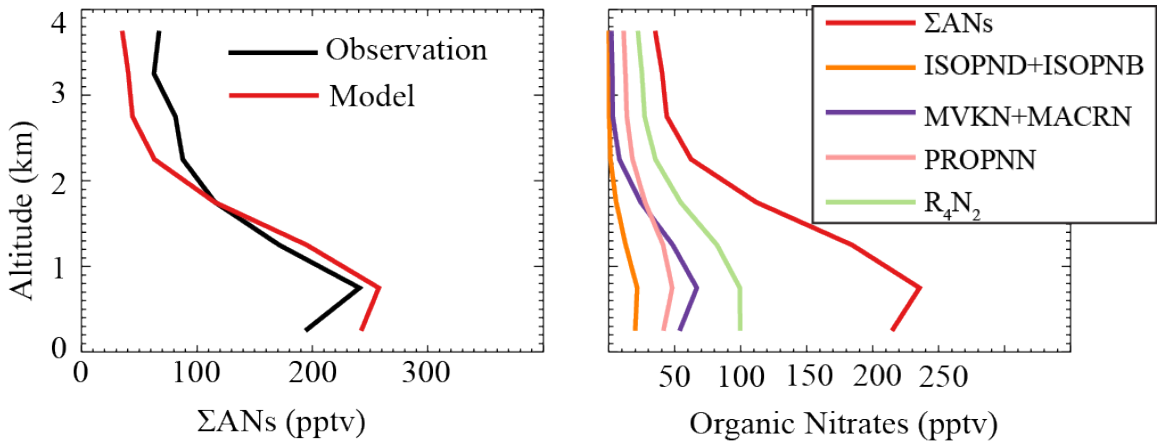
498 Figure 4 Ozone concentrations and ozone-CO correlations in the boundary layer (0 – 1.5
499 km) during ICARTT (July 1 – August 15, 2004). The top panels shows observed and
500 simulated values averaged over the 2° × 2.5° GEOS-Chem grid. The bottom left panel is
501 a model vs. observed scatterplot of these values. The bottom right panel shows the ozone-
502 CO correlations in the observations (black) and in the model (red). Regression slopes are
503 from a reduced-major-axis regression with errors determined by nonparametric bootstrap
504 resampling.



505

506 Figure 5 Mean vertical profiles of species concentrations during ICARTT (July 1st-Aug
507 15th 2004) over land (Figure 4). Measurements are from the DC-8 aircraft except for
508 MVK+MACR which was only measured aboard the WP-3D aircraft (we also show
509 isoprene from the WP-3D aircraft).

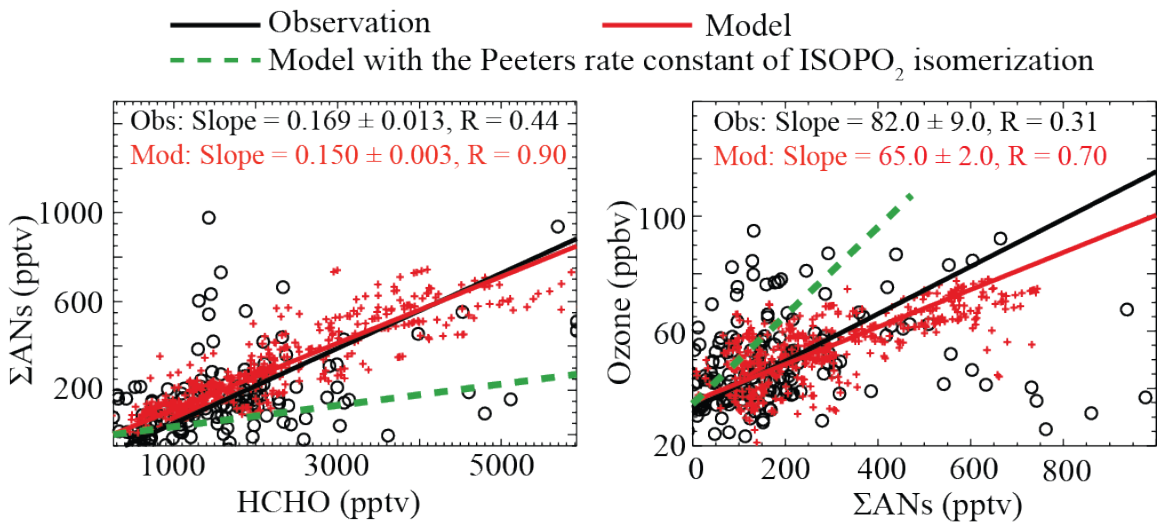
510



511

512 Figure 6 Left panel: mean vertical profiles of total organic nitrates excluding
513 peroxyacylnitrates (∑ANs) during ICARTT (July 1st-Aug 15th 2004) over land (Figure 4).
514 Observations (black) are compared to GEOS-Chem (red). Right panel: contributions of
515 individual species to mean ∑ANs in GEOS-Chem including β-hydroxyl isoprene nitrates
516 (ISOPNB), δ-hydroxyl isoprene nitrates (ISOPND), methacrolein nitrates (MACRN),
517 methylvinylketone nitrates (MVKN), propanone nitrate (PROPNN), and a lumped
518 organic nitrate (R_4N_2). R_4N_2 is produced from nighttime isoprene oxidation as well as
519 oxidation of $\geq C_3$ ketones, and $\geq C_4$ alkanes.

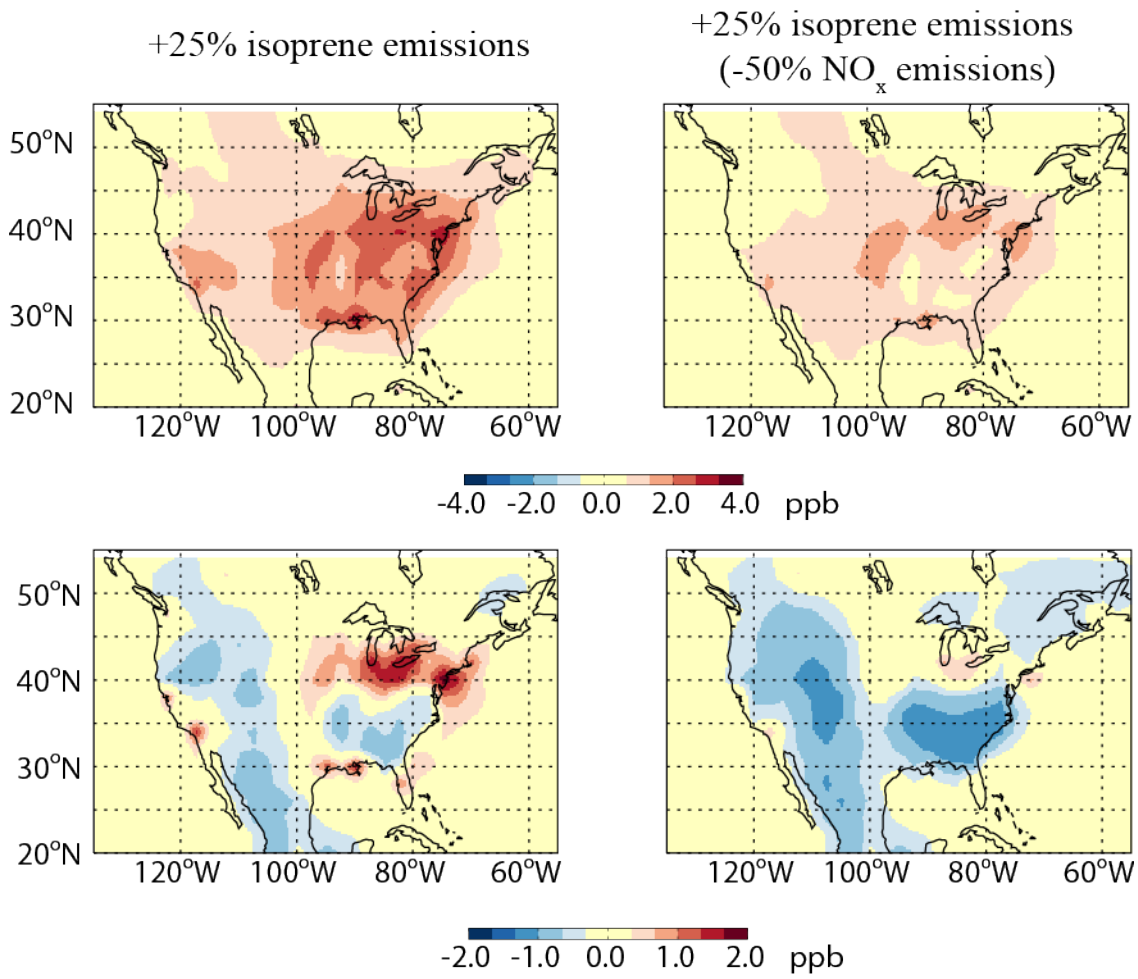
520



521

522 Figure 7 (left) ∑ANs vs. HCHO and ozone vs. ∑ANs correlations in the continental
523 boundary layer (<1.5 km) during ICARTT. Model results (red) are compared to
524 observations from the DC-8 aircraft (black). Solid lines are the reduced major axis
525 regression lines. Also shown is the model with a higher rate constant for $ISOPO_2$
526 isomerization following Peeters et al. (2009) (green dashed lines)..

527



528

529 Figure 8 Computed change of mean afternoon (1300 – 1700 LT) surface ozone
530 concentrations during July 2004 as a result of increasing isoprene emissions by 25% at
531 different levels of anthropogenic NO_x emissions. The top panels use the isoprene
532 oxidation mechanism in this work, and the bottom panels use the isoprene chemistry
533 applied in Zhang et al. (2011) that assumed a high yield of isoprene nitrates (18%)
534 without recycling of NO_x .

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Reference

Amos, H. M., Jacob, D. J., Holmes, C. D., Fisher, J. A., Wang, Q., Yantosca, R. M., Corbitt, E. S., Galarneau, E., Rutter, A. P., Gustin, M. S., Steffen, A., Schauer, J. J., Graydon, J. A., Louis, V. L. S., Talbot, R. W., Edgerton, E. S., Zhang, Y., and Sunderland, E. M.: Gas-particle partitioning of atmospheric Hg(II) and its effect on global mercury deposition, Atmos. Chem. Phys., 12, 591-603, 10.5194/acp-12-591-2012, 2012.

Atlas, E.: Evidence for [ge]C3 alkyl nitrates in rural and remote atmospheres, Nature, 331, 426-428, 1988.

Baker, J., Aschmann, S. M., Arey, J., and Atkinson, R.: Reactions of stabilized criegee intermediates from the gas-phase reactions of O3 with selected alkenes, Int. J. Chem. Kinet., 34, 73-85, 10.1002/kin.10022, 2002.

Barkley, M. P., Palmer, P. I., Ganzeveld, L., Arneth, A., Hagberg, D., Karl, T., Guenther, A., Paulot, F., Wennberg, P. O., Mao, J., Kurosu, T. P., Chance, K., Müller, J. F., De Smedt, I., Van Roozendael, M., Chen, D., Wang, Y., and Yantosca, R. M.: Can a "state of the art" chemistry transport model simulate Amazonian tropospheric chemistry?, J. Geophys. Res., 116, D16302, 10.1029/2011jd015893, 2011.

Beaver, M. R., Clair, J. M. S., Paulot, F., Spencer, K. M., Crounse, J. D., LaFranchi, B. W., Min, K. E., Pusede, S. E., Wooldridge, P. J., Schade, G. W., Park, C., Cohen, R. C., and Wennberg, P. O.: Importance of biogenic precursors to the budget of organic nitrates:

559 observations of multifunctional organic nitrates by CIMS and TD-LIF during BEARPEX
560 2009, Atmos. Chem. Phys., 12, 5773-5785, 10.5194/acp-12-5773-2012, 2012.

561 Bey, I., Jacob, D. J., Yantosca, R. M., Logan, J. A., Field, B. D., Fiore, A. M., Li, Q. B.,
562 Liu, H. G. Y., Mickley, L. J., and Schultz, M. G.: Global modeling of tropospheric
563 chemistry with assimilated meteorology: Model description and evaluation, J. Geophys.
564 Res.-Atmos., 106, 23073-23095, 2001.

565 Brown, S. S., deGouw, J. A., Warneke, C., Ryerson, T. B., Dubé, W. P., Atlas, E., Weber,
566 R. J., Peltier, R. E., Neuman, J. A., Roberts, J. M., Swanson, A., Flocke, F., McKeen, S.
567 A., Brioude, J., Sommariva, R., Trainer, M., Fehsenfeld, F. C., and Ravishankara, A. R.:
568 Nocturnal isoprene oxidation over the Northeast United States in summer and its impact
569 on reactive nitrogen partitioning and secondary organic aerosol, Atmos. Chem. Phys., 9,
570 3027-3042, 10.5194/acp-9-3027-2009, 2009.

571 Brown, S. S., and Stutz, J.: Nighttime radical observations and chemistry, Chemical
572 Society Reviews, 41, 6405-6447, 10.1039/C2CS35181A, 2012.

573 Browne, E. C., and Cohen, R. C.: Effects of biogenic nitrate chemistry on the NOx
574 lifetime in remote continental regions, Atmos. Chem. Phys., 12, 11917-11932,
575 10.5194/acp-12-11917-2012, 2012.

576 Carslaw, N., Creasey, D. J., Harrison, D., Heard, D. E., Hunter, M. C., Jacobs, P. J.,
577 Jenkin, M. E., Lee, J. D., Lewis, A. C., Pilling, M. J., Saunders, S. M., and Seakins, P. W.:
578 OH and HO2 radical chemistry in a forested region of north-western Greece, Atmos.
579 Environ., 35, 4725-4737, 2001.

580 Chin, M., Jacob, D. J., Munger, J. W., Parrish, D. D., and Doddridge, B. G.: Relationship
581 of ozone and carbon monoxide over North America, J. Geophys. Res., 99, 14565-14573,
582 10.1029/94jd00907, 1994.

583 Crounse, J. D., Paulot, F., Kjaergaard, H. G., and Wennberg, P. O.: Peroxy radical
584 isomerization in the oxidation of isoprene, Phys. Chem. Chem. Phys., 13, 13607-13613,
585 10.1039/C1CP21330J 2011.

586 Crounse, J. D., Knap, H. C., Ørnsø, K. B., Jørgensen, S., Paulot, F., Kjaergaard, H. G.,
587 and Wennberg, P. O.: Atmospheric Fate of Methacrolein. 1. Peroxy Radical
588 Isomerization Following Addition of OH and O2, The Journal of Physical Chemistry A,
589 116, 5756-5762, 10.1021/jp211560u, 2012.

590 Da Silva, G., Graham, C., and Wang, Z. F.: Unimolecular beta-Hydroxyperoxy Radical
591 Decomposition with OH Recycling in the Photochemical Oxidation of Isoprene, Environ.
592 Sci. Technol., 44, 250-256, 10.1021/es900924d, 2010.

593 Dillon, T. J., and Crowley, J. N.: Direct detection of OH formation in the reactions of
594 HO2 with CH3C(O)O-2 and other substituted peroxy radicals, Atmos. Chem. Phys., 8,
595 4877-4889, 2008.

596 Drury, E., Jacob, D. J., Spurr, R. J. D., Wang, J., Shinozuka, Y., Anderson, B. E., Clarke,
597 A. D., Dibb, J., McNaughton, C., and Weber, R.: Synthesis of satellite (MODIS), aircraft
598 (ICARTT), and surface (IMPROVE, EPA-AQS, AERONET) aerosol observations over
599 eastern North America to improve MODIS aerosol retrievals and constrain surface

aerosol concentrations and sources, J. Geophys. Res., 115, D14204, 10.1029/2009jd012629, 2010.

Farmer, D. K., Perring, A. E., Wooldridge, P. J., Blake, D. R., Baker, A., Meinardi, S., Huey, L. G., Tanner, D., Vargas, O., and Cohen, R. C.: Impact of organic nitrates on urban ozone production, Atmos. Chem. Phys., 11, 4085-4094, 10.5194/acp-11-4085-2011, 2011.

Fehsenfeld, F. C., Ancellet, G., Bates, T. S., Goldstein, A. H., Hardesty, R. M., Honrath, R., Law, K. S., Lewis, A. C., Leaitch, R., McKeen, S., Meagher, J., Parrish, D. D., Pszenny, A. A. P., Russell, P. B., Schlager, H., Seinfeld, J., Talbot, R., and Zbinden, R.: International Consortium for Atmospheric Research on Transport and Transformation (ICARTT): North America to Europe - Overview of the 2004 summer field study, J. Geophys. Res.-Atmos., 111, 10.1029/2006jd007829, 2006.

Fiore, A. M., Jacob, D. J., Bey, I., Yantosca, R. M., Field, B. D., Fusco, A. C., and Wilkinson, J. G.: Background ozone over the United States in summer: Origin, trend, and contribution to pollution episodes, J. Geophys. Res.-Atmos., 107, 4275 10.1029/2001jd000982, 2002.

Fiore, A. M., Horowitz, L. W., Purves, D. W., Levy, H., II, Evans, M. J., Wang, Y., Li, Q., and Yantosca, R. M.: Evaluating the contribution of changes in isoprene emissions to surface ozone trends over the eastern United States, J. Geophys. Res., 110, D12303, 10.1029/2004jd005485, 2005.

620 Fiore, A. M., Dentener, F. J., Wild, O., Cuvelier, C., Schultz, M. G., Hess, P., Textor, C.,
621 Schulz, M., Doherty, R. M., Horowitz, L. W., MacKenzie, I. A., Sanderson, M. G.,
622 Shindell, D. T., Stevenson, D. S., Szopa, S., Van Dingenen, R., Zeng, G., Atherton, C.,
623 Bergmann, D., Bey, I., Carmichael, G., Collins, W. J., Duncan, B. N., Faluvegi, G.,
624 Folberth, G., Gauss, M., Gong, S., Hauglustaine, D., Holloway, T., Isaksen, I. S. A.,
625 Jacob, D. J., Jonson, J. E., Kaminski, J. W., Keating, T. J., Lupu, A., Marmer, E.,
626 Montanaro, V., Park, R. J., Pitari, G., Pringle, K. J., Pyle, J. A., Schroeder, S., Vivanco,
627 M. G., Wind, P., Wojcik, G., Wu, S., and Zuber, A.: Multimodel estimates of
628 intercontinental source-receptor relationships for ozone pollution, J. Geophys. Res.-
629 Atmos., 114, 10.1029/2008jd010816, 2009.

630 Flocke, F., Volzthomas, A., and Kley, D.: Measurements of alkyl nitrates in rural and
631 polluted air masses, Atmospheric Environment Part a-General Topics, 25, 1951-1960,
632 10.1016/0960-1686(91)90276-d, 1991.

633 Fried, A., Walega, J. G., Olson, J. R., Crawford, J. H., Chen, G., Weibring, P., Richter, D.,
634 Roller, C., Tittel, F. K., Heikes, B. G., Snow, J. A., Shen, H. W., O'Sullivan, D. W.,
635 Porter, M., Fuelberg, H., Halland, J., and Millet, D. B.: Formaldehyde over North
636 America and the North Atlantic during the summer 2004 INTEX campaign: Methods,
637 observed distributions, and measurement-model comparisons, J. Geophys. Res.-Atmos.,
638 113, 10.1029/2007jd009185, 2008.

639 Fry, J. L., Kiendler-Scharr, A., Rollins, A. W., Brauers, T., Brown, S. S., Dorn, H. P.,
640 Dubé, W. P., Fuchs, H., Mensah, A., Rohrer, F., Tillmann, R., Wahner, A., Wooldridge,

641 P. J., and Cohen, R. C.: SOA from limonene: role of NO3 in its generation and
642 degradation, Atmos. Chem. Phys., 11, 3879-3894, 10.5194/acp-11-3879-2011, 2011.

643 Fu, T.-M., Jacob, D. J., and Heald, C. L.: Aqueous-phase reactive uptake of dicarbonyls
644 as a source of organic aerosol over eastern North America, Atmos. Environ., 43, 1814-
645 1822, http://dx.doi.org/10.1016/j.atmosenv.2008.12.029, 2009.

646 Giacopelli, P., Ford, K., Espada, C., and Shepson, P. B.: Comparison of the measured and
647 simulated isoprene nitrate distributions above a forest canopy, J. Geophys. Res.-Atmos.,
648 110, 10.1029/2004jd005123, 2005.

649 Gross, S., Iannone, R., Xiao, S., and Bertram, A. K.: Reactive uptake studies of NO3 and
650 N2O5 on alkenoic acid, alkanoate, and polyalcohol substrates to probe nighttime aerosol
651 chemistry, Phys. Chem. Chem. Phys., 11, 7792-7803, 2009.

652 Grossenbacher, J. W., Couch, T., Shepson, P. B., Thornberry, T., Witmer-Rich, M.,
653 Carroll, M. A., Faloona, I., Tan, D., Brune, W., Ostling, K., and Bertman, S.:
654 Measurements of isoprene nitrates above a forest canopy, Journal of Geophysical
655 Research: Atmospheres, 106, 24429-24438, 10.1029/2001jd900029, 2001.

656 Guenther, A., Karl, T., Harley, P., Wiedinmyer, C., Palmer, P. I., and Geron, C.:
657 Estimates of global terrestrial isoprene emissions using MEGAN (Model of Emissions of
658 Gases and Aerosols from Nature), Atmos. Chem. Phys., 6, 3181-3210, 2006.

659 Hasson, A. S., Tyndall, G. S., and Orlando, J. J.: A product yield study of the reaction of
660 HO2 radicals with ethyl peroxy (C2H5O2), acetyl peroxy (CH3C(O)O-2), and acetonyl

peroxy (CH3C(O)CH2O2) radicals, J. Phys. Chem. A, 108, 5979-5989, 10.1021/jp048873t, 2004.

Heald, C. L., Jacob, D. J., Park, R. J., Alexander, B., Fairlie, T. D., Yantosca, R. M., and Chu, D. A.: Transpacific transport of Asian anthropogenic aerosols and its impact on surface air quality in the United States, J. Geophys. Res.-Atmos., 111, 10.1029/2005jd006847, 2006.

Heald, C. L., Wilkinson, M. J., Monson, R. K., Alo, C. A., Wang, G., and Guenther, A.: Response of isoprene emission to ambient CO2 changes and implications for global budgets, Global Change Biology, 15, 1127-1140, 10.1111/j.1365-2486.2008.01802.x, 2009.

Hofzumahaus, A., Rohrer, F., Lu, K. D., Bohn, B., Brauers, T., Chang, C. C., Fuchs, H., Holland, F., Kita, K., Kondo, Y., Li, X., Lou, S. R., Shao, M., Zeng, L. M., Wahner, A., and Zhang, Y. H.: Amplified Trace Gas Removal in the Troposphere, Science, 324, 1702-1704, 10.1126/science.1164566, 2009.

Holtslag, A. A. M., and Boville, B. A.: Local Versus Nonlocal Boundary-Layer Diffusion in a Global Climate Model, Journal of Climate, 6, 1825-1842, 10.1175/1520-0442(1993)006<1825:lvnbld>2.0.co;2, 1993.

Horowitz, L. W., Liang, J. Y., Gardner, G. M., and Jacob, D. J.: Export of reactive nitrogen from North America during summertime: Sensitivity to hydrocarbon chemistry, J. Geophys. Res.-Atmos., 103, 13451-13476, 1998.

681 Horowitz, L. W., Fiore, A. M., Milly, G. P., Cohen, R. C., Perring, A., Wooldridge, P. J.,
682 Hess, P. G., Emmons, L. K., and Lamarque, J. F.: Observational constraints on the
683 chemistry of isoprene nitrates over the eastern United States, J. Geophys. Res.-Atmos.,
684 112, 10.1029/2006jd007747, 2007.

685 Hudman, R. C., Jacob, D. J., Turquety, S., Leibensperger, E. M., Murray, L. T., Wu, S.,
686 Gilliland, A. B., Avery, M., Bertram, T. H., Brune, W., Cohen, R. C., Dibb, J. E., Flocke,
687 F. M., Fried, A., Holloway, J., Neuman, J. A., Orville, R., Perring, A., Ren, X., Sachse, G.
688 W., Singh, H. B., Swanson, A., and Wooldridge, P. J.: Surface and lightning sources of
689 nitrogen oxides over the United States: Magnitudes, chemical evolution, and outflow, J.
690 Geophys. Res.-Atmos., 112, D12s05
691 Artn d12s05, 2007.

692 Hudman, R. C., Murray, L. T., Jacob, D. J., Millet, D. B., Turquety, S., Wu, S., Blake, D.
693 R., Goldstein, A. H., Holloway, J., and Sachse, G. W.: Biogenic versus anthropogenic
694 sources of CO in the United States, Geophys. Res. Lett., 35, L04801
695 Artn l04801, 2008.

696 Hudman, R. C., Murray, L. T., Jacob, D. J., Turquety, S., Wu, S., Millet, D. B., Avery,
697 M., Goldstein, A. H., and Holloway, J.: North American influence on tropospheric ozone
698 and the effects of recent emission reductions: Constraints from ICARTT observations, J.
699 Geophys. Res.-Atmos., 114, 10.1029/2008jd010126, 2009.

700 Ito, A., Sillman, S., and Penner, J. E.: Global chemical transport model study of ozone
701 response to changes in chemical kinetics and biogenic volatile organic compounds

emissions due to increasing temperatures: Sensitivities to isoprene nitrate chemistry and grid resolution, J. Geophys. Res.-Atmos., 114, 10.1029/2008jd011254, 2009.

Jacob, D. J., and Wofsy, S. C.: Photochemistry of Biogenic Emissions Over the Amazon Forest, J. Geophys. Res., 93, 1477-1486, 10.1029/JD093iD02p01477, 1988.

Jacob, D. J., Logan, J. A., Yevich, R. M., Gardner, G. M., Spivakovsky, C. M., Wofsy, S. C., Munger, J. W., Sillman, S., Prather, M. J., Rodgers, M. O., Westberg, H., and Zimmerman, P. R.: Simulation of summertime ozone over North America, Journal of Geophysical Research: Atmospheres, 98, 14797-14816, 10.1029/93jd01223, 1993.

Jenkin, M. E., Saunders, S. M., and Pilling, M. J.: The tropospheric degradation of volatile organic compounds: a protocol for mechanism development, Atmos. Environ., 31, 81-104, http://dx.doi.org/10.1016/S1352-2310(96)00105-7, 1997.

Jenkin, M. E., Hurley, M. D., and Wallington, T. J.: Investigation of the radical product channel of the CH3C(O)O-2+HO2 reaction in the gas phase, Phys. Chem. Chem. Phys., 9, 3149-3162, 10.1039/b702757e, 2007.

Karl, T., Harley, P., Emmons, L., Thornton, B., Guenther, A., Basu, C., Turnipseed, A., and Jardine, K.: Efficient Atmospheric Cleansing of Oxidized Organic Trace Gases by Vegetation, Science, 330, 816-819, 10.1126/science.1192534, 2010.

Kuhns, H., Knipping, E. M., and Vukovich, J. M.: Development of a United States–Mexico Emissions Inventory for the Big Bend Regional Aerosol and Visibility Observational (BRAVO) Study, J. Air Waste Manage. Assoc., 55, 677-692, 10.1080/10473289.2005.10464648, 2005.

723 Kwan, A. J., Chan, A. W. H., Ng, N. L., Kjaergaard, H. G., Seinfeld, J. H., and Wennberg,
724 P. O.: Peroxy radical chemistry and OH radical production during the NO3-initiated
725 oxidation of isoprene, Atmos. Chem. Phys., 12, 7499-7515, 10.5194/acp-12-7499-2012,
726 2012.

727 LaFranchi, B. W., Pétron, G., Miller, J. B., Lehman, S. J., Andrews, A. E., Dlugokencky,
728 E. J., Miller, B. R., Montzka, S. A., Hall, B., Neff, W., Sweeney, C., Turnbull, J. C.,
729 Wolfe, D. E., Tans, P. P., Gurney, K. R., and Guilderson, T. P.: Constraints on emissions
730 of carbon monoxide, methane, and a suite of hydrocarbons in the Colorado Front Range
731 using observations of 14CO2, Atmos. Chem. Phys. Discuss., 13, 1609-1672,
732 10.5194/acpd-13-1609-2013, 2013.

733 Lee, L., Wooldridge, P., Nah, T., Wilson, K., and Cohen, R.: Observation of rates and
734 products in the reaction of NO3 with submicron squalane and squalene aerosol, Phys.
735 Chem. Chem. Phys., 15, 882-892, 2013.

736 Lelieveld, J., Butler, T. M., Crowley, J. N., Dillon, T. J., Fischer, H., Ganzeveld, L.,
737 Harder, H., Lawrence, M. G., Martinez, M., Taraborrelli, D., and Williams, J.:
738 Atmospheric oxidation capacity sustained by a tropical forest, Nature, 452, 737-740,
739 10.1038/nature06870, 2008.

740 Liang, Q., Jaegle, L., Hudman, R. C., Turquety, S., Jacob, D. J., Avery, M. A., Browell, E.
741 V., Sachse, G. W., Blake, D. R., Brune, W., Ren, X., Cohen, R. C., Dibb, J. E., Fried, A.,
742 Fuelberg, H., Porter, M., Heikes, B. G., Huey, G., Singh, H. B., and Wennberg, P. O.:
743 Summertime influence of Asian pollution in the free troposphere over North America, J.
744 Geophys. Res.-Atmos., 112, D12s11

745 10.1029/2006jd007919, 2007.

746 Lin, J.-T., Youn, D., Liang, X.-Z., and Wuebbles, D. J.: Global model simulation of
747 summertime U.S. ozone diurnal cycle and its sensitivity to PBL mixing, spatial resolution,
748 and emissions, Atmos. Environ., 42, 8470-8483,
749 http://dx.doi.org/10.1016/j.atmosenv.2008.08.012, 2008.

750 Lin, J.-T., and McElroy, M. B.: Impacts of boundary layer mixing on pollutant vertical
751 profiles in the lower troposphere: Implications to satellite remote sensing, Atmos.
752 Environ., 44, 1726-1739, 10.1016/j.atmosenv.2010.02.009, 2010.

753 Liu, H. Y., Jacob, D. J., Bey, I., and Yantosca, R. M.: Constraints from Pb-210 and Be-7
754 on wet deposition and transport in a global three-dimensional chemical tracer model
755 driven by assimilated meteorological fields, J. Geophys. Res.-Atmos., 106, 12109-12128,
756 2001.

757 Liu, Y. J., Herdlinger-Blatt, I., McKinney, K. A., and Martin, S. T.: Production of methyl
758 vinyl ketone and methacrolein via the hydroperoxyl pathway of isoprene oxidation,
759 Atmos. Chem. Phys. Discuss., 12, 33323-33358, 10.5194/acpd-12-33323-2012, 2012.

760 Lockwood, A. L., Shepson, P. B., Fiddler, M. N., and Alaghmand, M.: Isoprene nitrates:
761 preparation, separation, identification, yields, and atmospheric chemistry, Atmos. Chem.
762 Phys., 10, 6169-6178, 10.5194/acp-10-6169-2010, 2010.

763 Mao, J., Jacob, D. J., Evans, M. J., Olson, J. R., Ren, X., Brune, W. H., Clair, J. M. S.,
764 Crounse, J. D., Spencer, K. M., Beaver, M. R., Wennberg, P. O., Cubison, M. J., Jimenez,
765 J. L., Fried, A., Weibring, P., Walega, J. G., Hall, S. R., Weinheimer, A. J., Cohen, R. C.,

766 Chen, G., Crawford, J. H., Jaeglé, L., Fisher, J. A., Yantosca, R. M., Le Sager, P., and
767 Carouge, C.: Chemistry of hydrogen oxide radicals (HOx) in the Arctic troposphere in
768 spring, Atmos. Chem. Phys. Discuss., 10, 6955-6994, 2010.

769 Mao, J., Ren, X., Zhang, L., Van Duin, D. M., Cohen, R. C., Park, J. H., Goldstein, A. H.,
770 Paulot, F., Beaver, M. R., Crounse, J. D., Wennberg, P. O., DiGangi, J. P., Henry, S. B.,
771 Keutsch, F. N., Park, C., Schade, G. W., Wolfe, G. M., Thornton, J. A., and Brune, W. H.:
772 Insights into hydroxyl measurements and atmospheric oxidation in a California forest,
773 Atmos. Chem. Phys., 12, 8009-8020, 10.5194/acp-12-8009-2012, 2012.

774 Mao, J., Fan, S., Jacob, D. J., and Travis, K. R.: Radical loss in the atmosphere from Cu-
775 Fe redox coupling in aerosols, Atmos. Chem. Phys., 13, 509-519, 10.5194/acp-13-509-
776 2013, 2013.

777 Marais, E. A., Jacob, D. J., Kurosu, T. P., Chance, K., Murphy, J. G., Reeves, C., Mills,
778 G., Casadio, S., Millet, D. B., Barkley, M. P., Paulot, F., and Mao, J.: Isoprene emissions
779 in Africa inferred from OMI observations of formaldehyde columns, Atmos. Chem. Phys.,
780 12, 6219-6235, 10.5194/acp-12-6219-2012, 2012.

781 Martin, R. V., Sauvage, B., Folkins, I., Sioris, C. E., Boone, C., Bernath, P., and Ziemke,
782 J.: Space-based constraints on the production of nitric oxide by lightning, J. Geophys.
783 Res.-Atmos., 112, D09309
784 10.1029/2006jd007831, 2007.

785 McLinden, C. A., Olsen, S. C., Hannegan, B., Wild, O., Prather, M. J., and Sundet, J.:
786 Stratospheric ozone in 3-D models: A simple chemistry and the cross-tropopause flux, J.
787 Geophys. Res.-Atmos., 105, 14653-14665, 2000.

788 Mickley, L. J., Jacob, D. J., and Rind, D.: Uncertainty in preindustrial abundance of
789 tropospheric ozone: Implications for radiative forcing calculations, J. Geophys. Res., 106,
790 3389-3399, 10.1029/2000jd900594, 2001.

791 Miller, J. B., Lehman, S. J., Montzka, S. A., Sweeney, C., Miller, B. R., Karion, A.,
792 Wolak, C., Dlugokencky, E. J., Southon, J., Turnbull, J. C., and Tans, P. P.: Linking
793 emissions of fossil fuel CO2 and other anthropogenic trace gases using atmospheric
794 14CO2, Journal of Geophysical Research: Atmospheres, 117, n/a-n/a,
795 10.1029/2011jd017048, 2012.

796 Miller, S. M., Matross, D. M., Andrews, A. E., Millet, D. B., Longo, M., Gottlieb, E. W.,
797 Hirsch, A. I., Gerbig, C., Lin, J. C., Daube, B. C., Hudman, R. C., Dias, P. L. S., Chow, V.
798 Y., and Wofsy, S. C.: Sources of carbon monoxide and formaldehyde in North America
799 determined from high-resolution atmospheric data, Atmos. Chem. Phys., 8, 7673-7696,
800 10.5194/acp-8-7673-2008, 2008.

801 Millet, D. B., Jacob, D. J., Turquety, S., Hudman, R. C., Wu, S. L., Fried, A., Walega, J.,
802 Heikes, B. G., Blake, D. R., Singh, H. B., Anderson, B. E., and Clarke, A. D.:
803 Formaldehyde distribution over North America: Implications for satellite retrievals of
804 formaldehyde columns and isoprene emission, J. Geophys. Res.-Atmos., 111, D24s02
805 10.1029/2005jd006853, 2006.

Millet, D. B., Jacob, D. J., Boersma, K. F., Fu, T.-M., Kurosu, T. P., Chance, K., Heald, C. L., and Guenther, A.: Spatial distribution of isoprene emissions from North America derived from formaldehyde column measurements by the OMI satellite sensor, J. Geophys. Res., 113, D02307, 10.1029/2007jd008950, 2008.

Murazaki, K., and Hess, P.: How does climate change contribute to surface ozone change over the United States?, J. Geophys. Res., 111, D05301, 10.1029/2005jd005873, 2006.

Murray, L. T., Jacob, D. J., Logan, J. A., Hudman, R. C., and Koshak, W. J.: Optimized regional and interannual variability of lightning in a global chemical transport model constrained by LIS/OTD satellite data, J. Geophys. Res., 117, D20307, 10.1029/2012jd017934, 2012.

Myneni, R. B., Yang, W., Nemani, R. R., Huete, A. R., Dickinson, R. E., Knyazikhin, Y., Didan, K., Fu, R., Negrón Juárez, R. I., Saatchi, S. S., Hashimoto, H., Ichii, K., Shabanov, N. V., Tan, B., Ratana, P., Privette, J. L., Morisette, J. T., Vermote, E. F., Roy, D. P., Wolfe, R. E., Friedl, M. A., Running, S. W., Votava, P., El-Saleous, N., Devadiga, S., Su, Y., and Salomonson, V. V.: Large seasonal swings in leaf area of Amazon rainforests, Proceedings of the National Academy of Sciences, 104, 4820-4823, 10.1073/pnas.0611338104, 2007.

Neff, J., Holland, E., Dentener, F., McDowell, W., and Russell, K.: The origin, composition and rates of organic nitrogen deposition: A missing piece of the nitrogen cycle?, Biogeochemistry, 57-58, 99-136, 10.1023/a:1015791622742, 2002.

826 Olivier, J., and Berdowski, J.: Global emission sources and sinks in "The Climate
827 System" edited by Berdowski, J., Guicherit, R. and B.J. Heij A.A. Balkema
828 Publishers/Swets & Zeitlinger Publishers, Lisse, The Netherlands, 33-78, 2001.

829 Parrella, J. P., Jacob, D. J., Liang, Q., Zhang, Y., Mickley, L. J., Miller, B., Evans, M. J.,
830 Yang, X., Pyle, J. A., Theys, N., and Van Roozendael, M.: Tropospheric bromine
831 chemistry: implications for present and pre-industrial ozone and mercury, Atmos. Chem.
832 Phys., 12, 6723-6740, 10.5194/acp-12-6723-2012, 2012.

833 Parrish, D. D., Trainer, M., Holloway, J. S., Yee, J. E., Warshawsky, M. S., Fehsenfeld, F.
834 C., Forbes, G. L., and Moody, J. L.: Relationships between ozone and carbon monoxide
835 at surface sites in the North Atlantic region, J. Geophys. Res., 103, 13357-13376,
836 10.1029/98jd00376, 1998.

837 Parrish, D. D.: Critical evaluation of US on-road vehicle emission inventories, Atmos.
838 Environ., 40, 2288-2300, http://dx.doi.org/10.1016/j.atmosenv.2005.11.033, 2006.

839 Patchen, A. K., Pennino, M. J., Kiep, A. C., and Elrod, M. J.: Direct kinetics study of the
840 product-forming channels of the reaction of isoprene-derived hydroxyperoxy radicals
841 with NO, Int. J. Chem. Kinet., 39, 353-361, 10.1002/kin.20248, 2007.

842 Paulot, F., Crounse, J. D., Kjaergaard, H. G., Kroll, J. H., Seinfeld, J. H., and Wennberg,
843 P. O.: Isoprene photooxidation: new insights into the production of acids and organic
844 nitrates, Atmos. Chem. Phys., 9, 1479-1501, 2009a.

Paulot, F., Crounse, J. D., Kjaergaard, H. G., Kurten, A., St Clair, J. M., Seinfeld, J. H., and Wennberg, P. O.: Unexpected Epoxide Formation in the Gas-Phase Photooxidation of Isoprene, Science, 325, 730-733, 10.1126/science.1172910, 2009b.

Paulot, F., Henze, D. K., and Wennberg, P. O.: Impact of the isoprene photochemical cascade on tropical ozone, Atmos. Chem. Phys., 12, 1307-1325, 10.5194/acp-12-1307-2012, 2012.

Paulson, S. E., and Seinfeld, J. H.: Development and evaluation of a photooxidation mechanism for isoprene, J. Geophys. Res.-Atmos., 97, 20703-20715, 1992.

Peeters, J., Nguyen, T. L., and Vereecken, L.: HOx radical regeneration in the oxidation of isoprene, Phys. Chem. Chem. Phys., 11, 5935-5939, 10.1039/b908511d, 2009.

Peeters, J., and Müller, J. F.: HOx radical regeneration in isoprene oxidation via peroxy radical isomerisations. II: experimental evidence and global impact, Phys. Chem. Chem. Phys., 12, 14227-14235, 10.1039/c0cp00811g, 2010.

Perring, A. E., Bertram, T. H., Wooldridge, P. J., Fried, A., Heikes, B. G., Dibb, J., Crounse, J. D., Wennberg, P. O., Blake, N. J., Blake, D. R., Brune, W. H., Singh, H. B., and Cohen, R. C.: Airborne observations of total RONO2: new constraints on the yield and lifetime of isoprene nitrates, Atmos. Chem. Phys., 9, 1451-1463, 2009a.

Perring, A. E., Wisthaler, A., Graus, M., Wooldridge, P. J., Lockwood, A. L., Mielke, L. H., Shepson, P. B., Hansel, A., and Cohen, R. C.: A product study of the isoprene+NO3 reaction, Atmos. Chem. Phys., 9, 4945-4956, 10.5194/acp-9-4945-2009, 2009b.

865 Perring, A. E., Bertram, T. H., Farmer, D. K., Wooldridge, P. J., Dibb, J., Blake, N. J.,
866 Blake, D. R., Singh, H. B., Fuelberg, H., Diskin, G., Sachse, G., and Cohen, R. C.: The
867 production and persistence of Sigma RONO(2) in the Mexico City plume, Atmos. Chem.
868 Phys., 10, 7215-7229, 10.5194/acp-10-7215-2010, 2010.

869 Pfister, G. G., Emmons, L. K., Hess, P. G., Lamarque, J. F., Thompson, A. M., and Yorks,
870 J. E.: Analysis of the Summer 2004 ozone budget over the United States using
871 Intercontinental Transport Experiment Ozonesonde Network Study (IONS) observations
872 and Model of Ozone and Related Tracers (MOZART-4) simulations, Journal of
873 Geophysical Research: Atmospheres, 113, D23306, 10.1029/2008jd010190, 2008.

874 Pratt, K. A., Mielke, L. H., Shepson, P. B., Bryan, A. M., Steiner, A. L., Ortega, J., Daly,
875 R., Helmig, D., Vogel, C. S., Griffith, S., Dusanter, S., Stevens, P. S., and Alaghmand,
876 M.: Contributions of individual reactive biogenic volatile organic compounds to organic
877 nitrates above a mixed forest, Atmos. Chem. Phys. Discuss., 12, 17031-17086,
878 10.5194/acpd-12-17031-2012, 2012.

879 Pugh, T. A. M., MacKenzie, A. R., Hewitt, C. N., Langford, B., Edwards, P. M.,
880 Furneaux, K. L., Heard, D. E., Hopkins, J. R., Jones, C. E., Karunaharan, A., Lee, J.,
881 Mills, G., Misztal, P., Moller, S., Monks, P. S., and Whalley, L. K.: Simulating
882 atmospheric composition over a South-East Asian tropical rainforest: performance of a
883 chemistry box model, Atmos. Chem. Phys., 10, 279-298, 2010.

884 Purves, D. W., Caspersen, J. P., Moorcroft, P. R., Hurtt, G. C., and Pacala, S. W.:
885 Human-induced changes in US biogenic volatile organic compound emissions: evidence

886 from long-term forest inventory data, Global Change Biology, 10, 1737-1755,
887 10.1111/j.1365-2486.2004.00844.x, 2004.

888 Rasmussen, D. J., Fiore, A. M., Naik, V., Horowitz, L. W., McGinnis, S. J., and Schultz,
889 M. G.: Surface ozone-temperature relationships in the eastern US: A monthly
890 climatology for evaluating chemistry-climate models, Atmos. Environ., 47, 142-153,
891 http://dx.doi.org/10.1016/j.atmosenv.2011.11.021, 2012.

892 Ren, X. R., Olson, J. R., Crawford, J. H., Brune, W. H., Mao, J. Q., Long, R. B., Chen, Z.,
893 Chen, G., Avery, M. A., Sachse, G. W., Barrick, J. D., Diskin, G. S., Huey, L. G., Fried,
894 A., Cohen, R. C., Heikes, B., Wennberg, P. O., Singh, H. B., Blake, D. R., and Shetter, R.
895 E.: HOx chemistry during INTEX-A 2004: Observation, model calculation, and
896 comparison with previous studies, J. Geophys. Res.-Atmos., 113, 13,
897 D05310,10.1029/2007jd009166, 2008.

898 Rollins, A. W., Kiendler-Scharr, A., Fry, J. L., Brauers, T., Brown, S. S., Dorn, H. P.,
899 Dubé, W. P., Fuchs, H., Mensah, A., Mentel, T. F., Rohrer, F., Tillmann, R., Wegener, R.,
900 Wooldridge, P. J., and Cohen, R. C.: Isoprene oxidation by nitrate radical: alkyl nitrate
901 and secondary organic aerosol yields, Atmos. Chem. Phys., 9, 6685-6703, 10.5194/acp-9-
902 6685-2009, 2009.

903 Rosen, R. S., Wood, E. C., Wooldridge, P. J., Thornton, J. A., Day, D. A., Kuster, W.,
904 Williams, E. J., Jobson, B. T., and Cohen, R. C.: Observations of total alkyl nitrates
905 during Texas Air Quality Study 2000: Implications for O-3 and alkyl nitrate
906 photochemistry, J. Geophys. Res.-Atmos., 109, 15, D07303,10.1029/2003jd004227, 2004.

907 Russo, R. S., Zhou, Y., Haase, K. B., Wingenter, O. W., Frinak, E. K., Mao, H., Talbot, R.
908 W., and Sive, B. C.: Temporal variability, sources, and sinks of C1-C5 alkyl nitrates in
909 coastal New England, Atmos. Chem. Phys., 10, 1865-1883, 10.5194/acp-10-1865-2010,
910 2010.

911 Sander, S. P., Abbatt, J. P. D., Barker, J. R., Burkholder, J. B., Friedl, R. R., Golden, D.
912 M., Huie, R. E., Kolb, C. E., Kurylo, M. J., Moortgat, G. K., Orkin, V. L., and Wine, P.
913 H.: Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies
914 Evaluation Number 17, JPL Publication 10-6, Jet Propulsion Laboratory, Pasadena, 2011.

915 Sanderson, M. G., Jones, C. D., Collins, W. J., Johnson, C. E., and Derwent, R. G.: Effect
916 of Climate Change on Isoprene Emissions and Surface Ozone Levels, Geophys. Res.
917 Lett., 30, 1936, 10.1029/2003gl017642, 2003.

918 Saunders, S. M., Jenkin, M. E., Derwent, R. G., and Pilling, M. J.: Protocol for the
919 development of the Master Chemical Mechanism, MCM v3 (Part A): tropospheric
920 degradation of non-aromatic volatile organic compounds, Atmos. Chem. Phys., 3, 161-
921 180, 2003.

922 Schultz, M., Backman, L., Balkanski, Y., Bjoerndalsaeter, S., Brand, R., Burrows, J.,
923 Dalsoeren, S., de Vasconcelos, M., Grodtmann, B., and Hauglustaine, D.: REanalysis of
924 the TROpospheric chemical composition over the past 40 years (RETRO)–A long-term
925 global modeling study of tropospheric chemistry, Final Report, Jülich/Hamburg,
926 Germany, 2007, 2007.

927 Singh, H. B., Brune, W. H., Crawford, J. H., Jacob, D. J., and Russell, P. B.: Overview of
928 the summer 2004 intercontinental chemical transport experiment - North America
929 (INTEX-A), J. Geophys. Res.-Atmos., 111, 10.1029/2006jd007905, 2006.

930 Sprengnether, M., Demerjian, K. L., Donahue, N. M., and Anderson, J. G.: Product
931 analysis of the OH oxidation of isoprene and 1,3-butadiene in the presence of NO, J.
932 Geophys. Res.-Atmos., 107, 10.1029/2001jd000716, 2002.

933 Stavrakou, T., Peeters, J., and Muller, J. F.: Improved global modelling of HOx recycling
934 in isoprene oxidation: evaluation against the GABRIEL and INTEX-A aircraft campaign
935 measurements, Atmos. Chem. Phys., 10, 9863-9878, 10.5194/acp-10-9863-2010, 2010.

936 Stone, D., Evans, M. J., Commane, R., Ingham, T., Floquet, C. F. A., McQuaid, J. B.,
937 Brookes, D. M., Monks, P. S., Purvis, R., Hamilton, J. F., Hopkins, J., Lee, J., Lewis, A.
938 C., Stewart, D., Murphy, J. G., Mills, G., Oram, D., Reeves, C. E., and Heard, D. E.: HOx
939 observations over West Africa during AMMA: impact of isoprene and NOx, Atmos.
940 Chem. Phys., 10, 9415-9429, 10.5194/acp-10-9415-2010, 2010.

941 Streets, D. G., Zhang, Q., Wang, L., He, K., Hao, J., Wu, Y., Tang, Y., and Carmichael,
942 G. R.: Revisiting China's CO emissions after the Transport and Chemical Evolution over
943 the Pacific (TRACE-P) mission: Synthesis of inventories, atmospheric modeling, and
944 observations, J. Geophys. Res., 111, D14306, 10.1029/2006jd007118, 2006.

945 Tan, D., Faloona, I., Simpas, J. B., Brune, W., Shepson, P. B., Couch, T. L., Sumner, A.
946 L., Carroll, M. A., Thornberry, T., Apel, E., Riemer, D., and Stockwell, W.: HOx budgets

947 in a deciduous forest: Results from the PROPHET summer 1998 campaign, J. Geophys.
948 Res.-Atmos., 106, 24407-24427, 2001.

949 Tang, M. J., Thieser, J., Schuster, G., and Crowley, J. N.: Uptake of NO3 and N2O5 to
950 Saharan dust, ambient urban aerosol and soot: a relative rate study, Atmos. Chem. Phys.,
951 10, 2965-2974, 10.5194/acp-10-2965-2010, 2010.

952 Thornton, J. A., Wooldridge, P. J., Cohen, R. C., Martinez, M., Harder, H., Brune, W. H.,
953 Williams, E. J., Roberts, J. M., Fehsenfeld, F. C., Hall, S. R., Shetter, R. E., Wert, B. P.,
954 and Fried, A.: Ozone production rates as a function of NOx abundances and HOx
955 production rates in the Nashville urban plume, J. Geophys. Res.-Atmos., 107, 17,
956 4146Artn 4146, 2002.

957 Turquety, S., Logan, J. A., Jacob, D. J., Hudman, R. C., Leung, F. Y., Heald, C. L.,
958 Yantosca, R. M., Wu, S., Emmons, L. K., Edwards, D. P., and Sachse, G. W.: Inventory
959 of boreal fire emissions for North America in 2004: Importance of peat burning and
960 pyroconvective injection, J. Geophys. Res.-Atmos., 112, D12s03
961 10.1029/2006jd007281, 2007.

962 van der Werf, G. R., Randerson, J. T., Giglio, L., Collatz, G. J., Mu, M., Kasibhatla, P. S.,
963 Morton, D. C., DeFries, R. S., Jin, Y., and van Leeuwen, T. T.: Global fire emissions and
964 the contribution of deforestation, savanna, forest, agricultural, and peat fires (1997–2009),
965 Atmos. Chem. Phys., 10, 11707-11735, 10.5194/acp-10-11707-2010, 2010.

966 van Donkelaar, A., Martin, R. V., Leaitch, W. R., Macdonald, A. M., Walker, T. W.,
967 Streets, D. G., Zhang, Q., Dunlea, E. J., Jimenez, J. L., Dibb, J. E., Huey, L. G., Weber,

R., and Andreae, M. O.: Analysis of aircraft and satellite measurements from the Intercontinental Chemical Transport Experiment (INTEX-B) to quantify long-range transport of East Asian sulfur to Canada, Atmos. Chem. Phys., 8, 2999-3014, 2008.

Vestreng, V., and Klein, H.: Emission data reported to UNECE/EMEP: Quality assurance and trend analysis & Presentation of WebDab, MSC-W Status Report, 2002.

von Kuhlmann, R., Lawrence, M. G., Poschl, U., and Crutzen, P. J.: Sensitivities in global scale modeling of isoprene, Atmos. Chem. Phys., 4, 1-17, 2004.

Wang, Y. H., Jacob, D. J., and Logan, J. A.: Global simulation of tropospheric O-3-NOx-hydrocarbon chemistry 1. Model formulation, J. Geophys. Res.-Atmos., 103, 10713-10725, 10.1029/98jd00158, 1998.

Warneke, C., McKeen, S. A., de Gouw, J. A., Goldan, P. D., Kuster, W. C., Holloway, J. S., Williams, E. J., Lerner, B. M., Parrish, D. D., Trainer, M., Fehsenfeld, F. C., Kato, S., Atlas, E. L., Baker, A., and Blake, D. R.: Determination of urban volatile organic compound emission ratios and comparison with an emissions database, J. Geophys. Res., 112, D10S47, 10.1029/2006jd007930, 2007.

Warneke, C., de Gouw, J. A., Del Negro, L., Brioude, J., McKeen, S., Stark, H., Kuster, W. C., Goldan, P. D., Trainer, M., Fehsenfeld, F. C., Wiedinmyer, C., Guenther, A. B., Hansel, A., Wisthaler, A., Atlas, E., Holloway, J. S., Ryerson, T. B., Peischl, J., Huey, L. G., and Hanks, A. T. C.: Biogenic emission measurement and inventories determination of biogenic emissions in the eastern United States and Texas and comparison with

biogenic emission inventories, J. Geophys. Res.-Atmos., 115, 10.1029/2009jd012445, 2010.

Wesely, M. L.: Parameterization of surface resistances to gaseous dry deposition in regional-scale numerical-models, Atmos. Environ., 23, 1293-1304, 1989.

Whalley, L. K., Edwards, P. M., Furneaux, K. L., Goddard, A., Ingham, T., Evans, M. J., Stone, D., Hopkins, J. R., Jones, C. E., Karunaharan, A., Lee, J. D., Lewis, A. C., Monks, P. S., Moller, S. J., and Heard, D. E.: Quantifying the magnitude of a missing hydroxyl radical source in a tropical rainforest, Atmos. Chem. Phys., 11, 7223-7233, 10.5194/acp-11-7223-2011, 2011.

Williams, J., Roberts, J. M., Fehsenfeld, F. C., Bertman, S. B., Buhr, M. P., Goldan, P. D., Hübler, G., Kuster, W. C., Ryerson, T. B., Trainer, M., and Young, V.: Regional ozone from biogenic hydrocarbons deduced from airborne measurements of PAN, PPN, and MPAN, Geophys. Res. Lett., 24, 1099-1102, 10.1029/97gl00548, 1997.

Wolfe, G. M., Crounse, J. D., Parrish, J. D., St. Clair, J. M., Beaver, M. R., Paulot, F., Yoon, T. P., Wennberg, P. O., and Keutsch, F. N.: Photolysis, OH reactivity and ozone reactivity of a proxy for isoprene-derived hydroperoxyenals (HPALDs), Phys. Chem. Chem. Phys., 14, 7276-7286, 10.1039/C2CP40388A, 2012.

Wu, S., Mickley, L. J., Jacob, D. J., Logan, J. A., Yantosca, R. M., and Rind, D.: Why are there large differences between models in global budgets of tropospheric ozone?, J. Geophys. Res., 112, D05302, 10.1029/2006jd007801, 2007.

1008 Wu, S., Mickley, L. J., Leibensperger, E. M., Jacob, D. J., Rind, D., and Streets, D. G.:
1009 Effects of 2000-2050 global change on ozone air quality in the United States, J. Geophys.
1010 Res., 113, D06302, 10.1029/2007jd008917, 2008.

1011 Wu, S., Mickley, L. J., Kaplan, J. O., and Jacob, D. J.: Impacts of changes in land use and
1012 land cover on atmospheric chemistry and air quality over the 21st century, Atmos. Chem.
1013 Phys., 12, 1597-1609, 10.5194/acp-12-1597-2012, 2012.

1014 Xie, Y., Paulot, F., Carter, W. P. L., Nolte, C. G., Luecken, D. J., Hutzell, W. T.,
1015 Wennberg, P. O., Cohen, R. C., and Pinder, R. W.: Understanding the impact of recent
1016 advances in isoprene photooxidation on simulations of regional air quality, Atmos. Chem.
1017 Phys. Discuss., 12, 27173-27218, 10.5194/acpd-12-27173-2012, 2012.

1018 Yienger, J. J., and Levy, H.: Empirical-model of global soil-biogenic NOx emissions, J.
1019 Geophys. Res.-Atmos., 100, 11447-11464, 10.1029/95jd00370, 1995.

1020 Yu, S., Mathur, R., Schere, K., Kang, D., Pleim, J., and Otte, T. L.: A detailed evaluation
1021 of the Eta-CMAQ forecast model performance for O3, its related precursors, and
1022 meteorological parameters during the 2004 ICARTT study, Journal of Geophysical
1023 Research: Atmospheres, 112, D12S14, 10.1029/2006jd007715, 2007.

1024 Yu, S., Mathur, R., Sarwar, G., Kang, D., Tong, D., Pouliot, G., and Pleim, J.: Eta-
1025 CMAQ air quality forecasts for O3 and related species using three different
1026 photochemical mechanisms (CB4, CB05, SAPRC-99): comparisons with measurements
1027 during the 2004 ICARTT study, Atmos. Chem. Phys., 10, 3001-3025, 10.5194/acp-10-
1028 3001-2010, 2010.

1029 Zhang, L., Jacob, D. J., Downey, N. V., Wood, D. A., Blewitt, D., Carouge, C. C., van
1030 Donkelaar, A., Jones, D. B. A., Murray, L. T., and Wang, Y.: Improved estimate of the
1031 policy-relevant background ozone in the United States using the GEOS-Chem global
1032 model with 1/2° × 2/3° horizontal resolution over North America, Atmos. Environ., 45,
1033 6769-6776, http://dx.doi.org/10.1016/j.atmosenv.2011.07.054, 2011.
1034